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ADDITIVES TO PREVENT DELETERIOUS EFFECTS ASSOCIATED WITH LONG-T--ETC(U)
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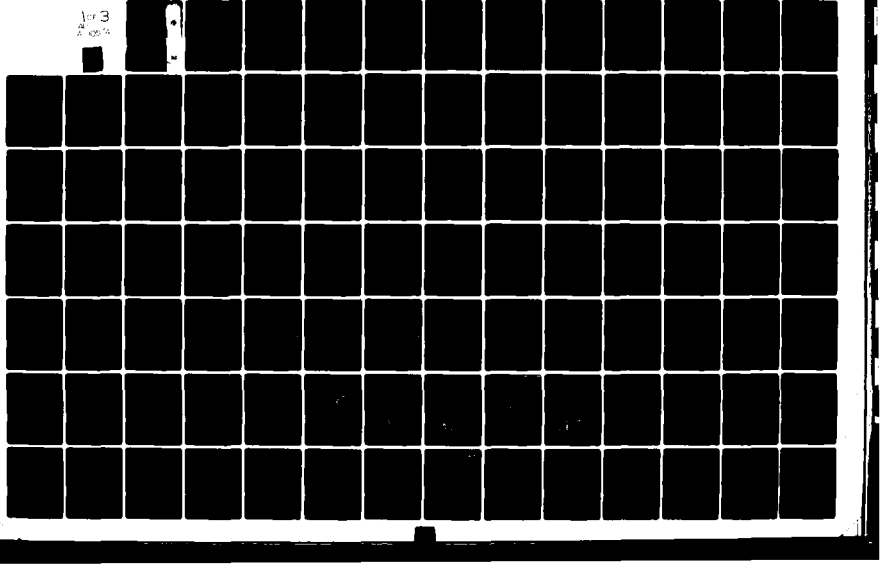

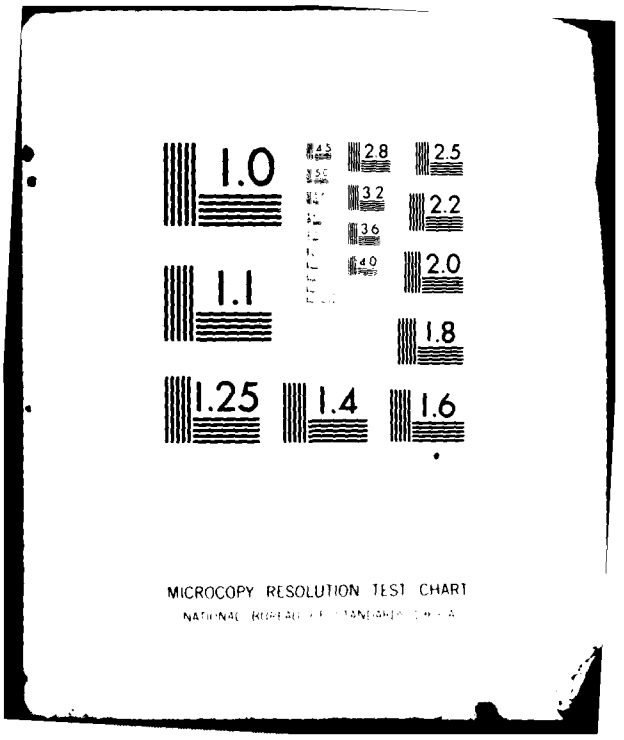
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LEVEL II

ADDITIVES TO PREVENT DELETERIOUS EFFECTS ASSOCIATED WITH LONG-TERM STORAGE OF PETROLEUM PRODUCTS

U.S. ARMY
CORPS OF ENGINEERS
HUNTSVILLE DIVISION

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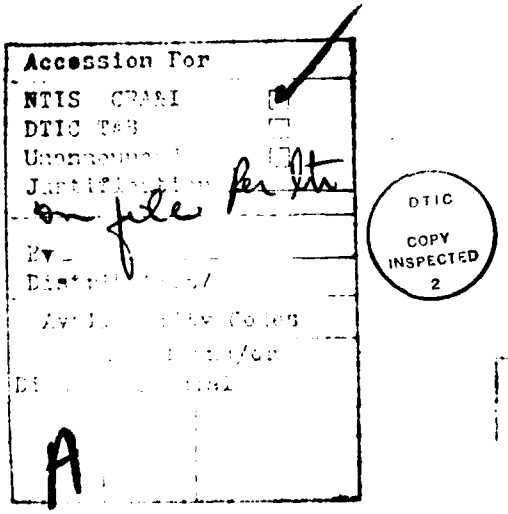

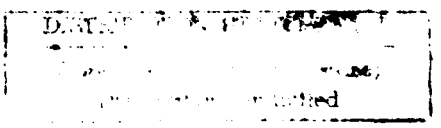

HNDTR-80-50-SP

Additives to Prevent Deleterious Effects Associated With Long-Term Storage of Petroleum Products

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September 1980

FOREWORD

This investigation was conducted during the period 17 March - 21 April 1980, by the Environmental Laboratory of the U.S. Army Engineer Waterways Experiment Station (WES) for U.S. Army Engineer Division, Huntsville.

This investigation was conducted to develop data that will assist engineers in the preparation of design criteria in support of Planning for the Regional and Noncontiguous Storage under the Strategic Petroleum Reserve Program for the Department of Energy. The Huntsville Division endorses the recommendations and findings of this report.

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ADDITIVES TO PREVENT DELETERIOUS EFFECTS ASSOCIATED WITH LONG-TERM STORAGE OF PETROLEUM PRODUCTS

PART I: INTRODUCTION

Background

1. Recent disruptions in the supply and distribution of petroleum products within the United States has aroused interest in systems for regional long-term storage of refined petroleum products. Crude oil surface and subsurface storage systems have both been considered. The major concern in storage systems is the long-term stability of the critical petroleum products and crude oil.

2. Most crude oil reserves are kept in the original reservoir formations. However, extraction, refining and distribition of these resources does not meet specific demands if portions of the process train are disrupted. It is therefore necessary to have several storage sites for strategic, regional reserves. The transportation and storage processes often increase instability and contamination problems in the refined products and crude. Mixing of products from diverse sources similarly can cause unique problems related to deterioration during long-term storage.

3. Only limited information regarding stability during long-term storage is available because production and marketing practices of the petroleum industry do not require such operations. Most storage is short-term because this is most economical in the present producer-consumer systems.

Objective

4. The objectives of the study are to present the deleterious effects of long-term storage of crude oil and petroleum products and to suggest products and process modifications which will minimize or eliminate the negative effects of such storage. Specific additives, treatment rates, and cost are provided when available.

Methodology

5. The literature was reviewed to evaluate the available information for data from theoretical and research studies to determine what means of treatment would prove to be most applicable. This review was supplemented by discussions with military and civilian experts familiar with the chemistry and stability of petroleum and additive compounds, and a compilation of information on currently marketed additives.

6. The criteria used in evaluating the potential of the various methods or processes found in the literature included: the anticipated ability of a process or additive to prevent significant deterioration of the product, the feasibility of the process or additive, the compatability of processes and additives and the deleterious effect of additive components on other storage parameters.

7. Laboratory testing of products was not within the tasks delineated for this study. All data supplied by manufacturers was accepted without additional testing or verification.

Scope

8. This report includes the results of the literature review, the specific literature available from commercial sources, preliminary cost estimates, a bibliography, and recommendations with regard to additional steps to evaluate stabilizing additives.

PART II: LONG-TERM EFFECTS OF PETROLEUM PRODUCT STORAGE

Major Deleterious Effects

9. The major problems that are associated with long-term storage of any petroleum or petroleum-derived material relate to changes in the molecular structure of the hydrocarbons (natural or biologically mediated), solid/liquid phase separations that can occur with the stored liquid, and rapid corrosion of surrounding metal or concrete due to microbially-accelerated, chemical attack. Major effects are generally classed as autoxidation, metal reactivity, pour point increase, sludge formation, bacterial activity, and corrosion.

Autoxidation

10. Autoxidation is a major problem of long-term bulk storage of petroleum fuels. The deterioration of the fuels in storage is a function of initial oxygen content, subsequent oxygen availability catalysts and duration of storage. The hydrocarbon type is also a factor. The most reactive compounds are diolefins followed in order of stability by aromatic olefins, aliphatic olefins, alkyl aromatics, naphthenes, and paraffins (Lundberg, 1962). The chain reaction decomposition occurs by a two-step method (Ducek, 1964; Walsh, 1947; Barnett, 1957; Medley, et al., 1960). Hydrocarbons reacting with atmospheric oxygen initially produce alkyl or aryl hydroperoxides (Walsh, 1947; Lundberg, 1961; Kennerly, et al., 1952; Boozer, et al., 1955). The hydroperoxides react producing secondary oxidation products such as aldehydes, ketones, hemiacetals, and esters (Ducek, 1964). These later oxidation products eventually form insoluable gums. The hydroperoxide disassociation is accelerated by heavy metal catalysts.

Metal reactivity

11. Metal deactivator additives inhibit the pro-oxidant catalytic activity of metals such as copper and its compounds. These metals promote degenerative chain branching of the hydrocarbons, thereby enhancing oxidation and polymerization. Corrosive elements such as vanadium can also be treated to render them inactive.

Pour point increasing

12. The tendency of pour points to increase with time is dependent upon the crystallization of wax. The formation of wax can alter pumpability of a

product and virtually solidify an entire mass if wax content is sufficiently high. Additives which modify the growth of crystals can sufficiently lower pour points so as to provide a product pumpable at temperatures below its normal pour point.

Sludge formation

13. All petroleum products exhibit sludge formation during storage. The precipitation of gums, resins, asphaltenes, water and suspended sediment often causes the plugging of pumps, lines, and filters. Dispersant additives prevent the precipitation of large quantities of the above listed materials by maintaining them in suspension.

Bacterial activity

14. Petroleum products are suceptable to bacterial degradation especially in the presence of a water/petroleum interface. Bacterial accumulations often produce a slime (large masses of bacteria) which can cause plugging of fuel handling systems. The waste product of bacteria growth is acidic and promotes the corrosion of storage facility materials. Retarding or eliminating bacterial activity prevents corrosion of metal parts, destruction of petroleum products, and prevents system fouling by slime accumulations.

Corrosion

15. The destructive attack of metal components of storage facilities by chemical or electrochemical reactions can be minimized by use of inhibitors. Organic inhibitors can be used in petroleum storage to effectively control corrosion. The inhibitors adsorb to metal surfaces forming a layer a monolayer thick. This layer blocks the discharge of hydrogen ion and dissolution of metal ions. The effectiveness of the polar molecules attached to the surface is a function of size, shape, charge and orientation of the molecule or group of molecules.

Materials to be Stored

Crude oil

16. Crude oil (Table 1) is being stored in various surface and subsurface facilities in several countries. Long-term storage of 7 to 10 years appears to have little effect on the crude, although a paucity of material testing makes verification difficult. In South Africa, emulsions at the oil-water interface

Table 1

Petroleum/Product Types and Characteristics

Characteristics	Crude Oil Type (Category) I	II	III	IV	V	VI
API Gravity (°API)	30-36	40-45	30-36	34-40	36-41	26-30
Total Sulphur (wt%) Max.	1.99	0.25	0.50	0.25	0.50	1.25
Pour Point (°F) Max.	50	50	50	50	50	50
Salt Content (lbs/1000 bbls) Max.	50	50	50	50	50	50
Viscosity (SUS @ 60°F) Max.	150	150	150	150	150	150
Reid Vapor Pressure (Psig @ 100°F) Max.	11	11	11	11	11	11
Mercaptans (PPM in 375-500°F) Max.	No limit	12	12	12	No limit	12
Yields (Vol. %)						
Naptha (375°F)	24-30	35-42	21-29	29-36	30-38	15-20
Distillate (375-620°F)	17-31	21-35	23-37	31-45	19-33	24-27
Gas Oil (620-1050°F)	26-38	20-34	28-42	20-34	23-37	38-42
Residuum (1050°F)	10-19	4-9	7-14	0-5	7-14	15-20
Water and Sediment (Vol. % Max.)	1.0	1.0	1.0	1.0	1.0	1.0

Note: Supplied by Huntsville Divison

apparently resulted from the use of centrifugal pumps for circulating water below the petroleum, but effects of storage on the oil are minimal. Underground storage of crude in Sweden is of moderate time duration (10 years). The crude is mixed by input and extraction procedures associated with normal delivery and use. Circulation of the oil and/or the water bed below the oil through heat exchangers also enhances mixing of new and old oil, and therefore limits average residence time of the stored crude. Sludge accumulation in the water bed is minimal which indicates only minor deterioration storage time. Information regarding physical and chemical alterations of other crudes stored in the U.S. and West Germany is unavailable or nonexistent.

Residual fuel oil

17. Crude oil at the well head contains a variety of contaminants both natural materials and materials added to enhance extraction from the reservoir. Among the contaminants and/or additives are dewaxers, corrosion inhibitors, emulsion breakers, naptha acids, drilling mud and related chemicals, dispersants and salts. Some of these contaminants remain in the crude through heaters, washers, and the crude-heating furnace. The result is that the contaminants often concentrate in the receiver tower and are extracted with the residual oil (Table 2). Analyses show various concentrations of iron, copper, sodium, nickel, calcium, vanadium, mangesium, barium, and aluminum are present in the residual oil.

18. Sludge deposition and the instability of the residual oil are major problems during storage. The fuel processing, oxidation, and polymerization produces insoluable compounds that precipitate as a sludge. Blending or mixing fuels from different processes or sources may produce the precipitation of asphaltenes, an additional sludge-forming problem.

19. Waxy components of light residual oils separate from the oil as it cools. These crystals can form a major phase separation if cooling continues for extensive periods of time. This separation affects the overall properties of the oil and may cause problems in regards to pumpability. The ASTM method for determination of minimum cold storage and handling temperatures is defined in ASTM D 3245, and addresses this tendency to form waxes (Bowden, et al., 1978).

20. Residual oils and crude are generally maintained at 50°-60°C during storage to facilitate extraction and prevent wax formation.

Table 2

General

No. 6 Oil Specification

Grade (ASTM)	6
Specific Gravity, 60/60°F	0.910-0.993
Saybolt Viscosity,	
Universal at 38°C (100°F)	---
Furol at 50°C (122°F)	(50-250)
Kinematic Viscosity, cSt	
At 38°C (100°F)	---
At 50°C (122°F)	(103-530)
Flash Point, °C (°F), Min.	66(150)
Four Point, °C (°F), Max.	16(60)
Ash, Wt %, Max.	0.1
Water and Sediment, by Centrifuge, Vol %, Max.	1.0
or:	
Water by Distillation, Vol %, Max.	1.0
and:	
Sediment by Extraction, Wt %, Max	0.1
Sulfur, Wt %, Max.	2.7
Compatibility Rating (D 2781), Max.	2
Ramsbottom Carbon Residue, Wt %, Max.	15
Asphaltenes (IP 143), Wt %, Max.	15
Additives	NONE

Note: Supplied by Huntsville Division.

Jet fuels

21. The storage stability of jet fuels (Table 3) is routinely evaluated and specified by existent and accelerated gum tests. Stringent requirements placed on jet fuel production by military and civilian specifications provide a fuel product which is relatively stable when antioxidant additives are incorporated.

22. Storage of jet fuel over a liquid brine bed in a rock salt cavity proved successful for a test period of 5 years. No measurable alteration of composition, acidity, tar, and sulfur content was observed. The fuels passed static thermal stability testing, but only passed marginally on dynamic tests. Sodium content after storage did not exceed that of certain commercially available fuels ($3.5 \quad 10^{-5}$ percent).

23. Oxygen content significantly affects thermal stability of the fuels. Fuels of inherent high thermal stability are less susceptable to the effects of oxygen, and therefore would require less antioxidant additive. The effect of temperature and duration of storage time has little effect on fuels if oxygen content is minimal and if temperatures are maintained below 55°C.

24. Soviet investigations of jet fuels from naphthenic petroleum indicate these fuels have more nitrogen bases (primarily alkyl derivatives of quinoline and pyridine) than those from paraffinic petroleums. The removal of nitrogen bases from both products significantly improved thermal stability and decreased eventual residue formation caused by oxidation. Another study revealed that only thermal stability changed significantly during long-term storage of hydrogenated fuels. This change could be curtailed by the addition of antioxidation or dispersing additives (Bowden, et al., 1978).

25. Jet fuels are such highly refined products that usually gum formation from thermal decomposition is the major deterioration problem. Modification of refining techniques and use of antioxidants appear to provide satisfactory stability in storage.

Naphtha

26. Naphtha or petroleum benzine is a mixture of low-boiling point fractions of petroleum. The mix consists chiefly of hydrocarbons of the methane series--principally pentones and hexanes. The boiling point is between 35° and 80°C. Naphtha is the principal feedstock for production of benzene cyclohexane, xylene, and gasoline.

Table 3

Detailed Requirements of Aviation Turbine Fuels

Property	Jet A or Jet A-1	Jet B
Acidity, total max, mg KOH/g	0.1	
Aromatics, vol, max, %	20	20
Sulfur, mercaptan, wt, max, %	0.003	0.003
Sulfur, total wt, max, %	0.3	0.3
Distillation temperature, °F(C):		
10% recovered, max, temp	400(204.4)	--
20% recovered, max, temp	--	290(143.3)
50% recovered, max, temp	Report	370(187.8)
90% recovered, max, temp	Report	470(243.3)
Final boiling point, max, °F(°C)	572(300)	--
Distillation residue, max, %	1.5	1.5
Distillation loss, max, %	1.5	1.5
Flash point, min, °F(°C)	100(37.8)	--
Gravity, max, °API(min, sp gr) at 60°F	51(0.7753)	57(0.7507)
Gravity, min, °API(max, sp gr) at 60°F	37(0.8398)	45(0.8017)
Vapor pressure, max, lb	--	3
Freezing point, max, °C	-40 Jet A	-50
	-50 Jet A-1	--
Vixcosity -4°F (-20°C) max, cSt	8	--
Net heat of combustion, min, Btu/lb	18,400	18,400
Combustion properties: one of the following requirements shall be met:		
(1) Luminometer number, min or	45	45
(2) Smoke point, min or	25	25
(3) Smoke point, min and	20	20
Naphthalenes, vol, max, %	3	3
Corrosion, copper strip 2 h at 212°F(100°C) max	No. 1	No. 1
Thermal stability: one of the following requirements shall be met:		
(1) Filter pressure drop, max, in. Hg	3	3
Preheater deposit less than	Code 3	Code 3
(2) Filter pressure drop, max, mm Hg	25	25
Tube deposit less than	Code 3	Code 3
Existent gum, mg/100 ml, max	7	7
Water reaction:		
Separation rating, max	2	2
Interface rating, max	1b	1b
Additives (see 4.2)		
Electrical conductivity, pS/m	--	--

27. Because naphtha is a production intermediate very little information is available on stability in storage. In most cases, there seems to be no provision for long-term storage of naphtha and no available literature on the use of additives in stored naphtha. The most troublesome impurities are organic acids and ringed nitro compounds. The aromatic and parafenic types are both lighter than the residual oils and may be stored at temperatures as low as 30°F without gelling. Napthas can deteriorate as do other petroleum products, but little data is available on the deterioration due to extended duration of storage.

PART III: DISCUSSION

Antioxidants

28. Many petroleum fuels exposed to air in storage at ambient temperatures will undergo oxidation and some polymerization to form resinous materials referred to as gums. Alkenes or olefins (unsaturated hydrocarbons) autoxidize more rapidly than alkanes. The oxygen is thought to attack the carbon atom adjacent to the double bond in preference to other secondary or tertiary hydrogen atoms (see Figure 1). The hydroperoxide formed is converted to a free radical by thermal decomposition and the free radical then is available to initiate polymerization. Polymer formation usually terminates when two growing chains collide. Polymers formed in autoxidation usually have a random spatial arrangement of polymeric units and appears as oily, sticky semisolids. Light energy and dissolved metal accelerate gum formation.

29. The most effective inhibitors for autoxidation are phenylenediamenes and hindered phenols (Figure 2). The chain-breaking activity of these compounds is thought to be related to their ability to donate hydrogen atoms to the peroxy radical causing it to stabilize.

30. Experience with the use of antioxidants in long-term storage of petroleum products is limited. LePera (1966) noted that autoxidant depletion could be observed within 6 weeks in accelerated aging tests on gasoline.

31. Dupont Corporation (Appendix A) has reported tests where one of their alkylated phenol additives showed only 10 mg/100 ml gum after 9 weeks of storage at 43°C. This test simulated field storage for nine months and at the end of this time gum formations exceeded acceptable levels (7 mg/100 ml).

32. Ethyl Corporation has reported (Appendix A) that in 43°C storage tests with regular, leaded (7.5g Pb/US gallon as tetraethyl lead) gasoline their additive, Ethyl 733 performed so as to maintain acceptable gum levels (7 mg/100 ml) for 7 weeks. One week storage at 43°C is considered by Ethyl Corporation as equal to one month's storage in the field.

33. In other testing with full-boiling-range catalytically cracked gasoline, Ethyl 733 maintained acceptable gum levels for 36 weeks (43°C). Tests with blended fuels containing catalytically cracked, straight run and polymer gasolines showed that no increase in gum could be detected after

$$RCH{=}CHCH_2R + O_2 \longrightarrow RCH{=}CH\,\underset{\underset{O-OH}{|}}{CH}R$$

Alkene + Oxygen ⟶ Hydroperoxide

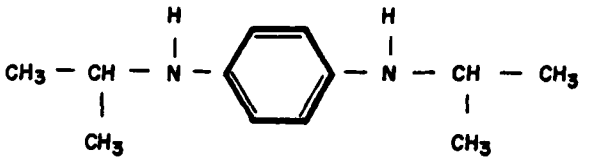
Thermal decomposition yields a free radical ($RO^{\bullet}$).

$$RO^{\bullet} + CH_2{=}CH_2 \longrightarrow RO-CH_2-CH_2^{\bullet}$$

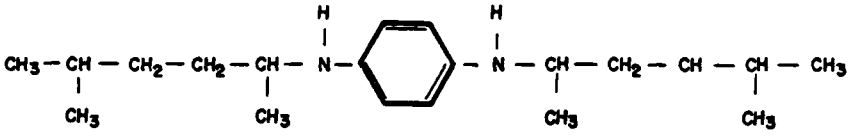
$$ROCH_2CH_2^{\bullet} + XCH_2{=}CH_2 \longrightarrow RO(CH_2CH_2)_x\ CH_2CH_2^{\bullet}$$

Propagation usually ends as growing chains collide.

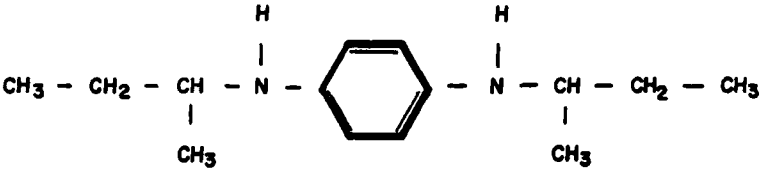
Figure 1. Chemical pathway involved in gum formation in stored petroleum products.



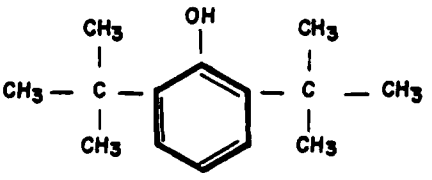
N, N'- Diisopropyl-p-phenylenediamine



N, N'-bis- (1, 4-dimethylpentyl)-p-phenylenediamine



N, N'-Di-sec-butyl-p-phenylenediamine



2, 6-di-tert-butylphenol

Figure 2. Compounds used as antioxidants in fuel storage.

20 weeks. No tests are available on Ethyl antioxidation additives in jet fuel although the same blend, Ethyl 733, is the suggested additive.

34. No information is presently available on use of antioxidant for long-term (10 to 20 years) storage of petroleum products. Most testing has been with gasolines and have simulated relatively short periods of storage. If antioxidants are to be employed for jet fuel storage, testing to determine maximum limits of effectiveness will be required.

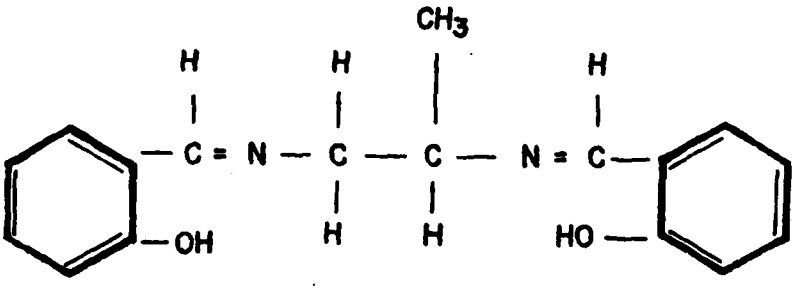
Metal Reactivity

35. Heavy metals (including copper, cadmium, mercury, and uncombined lead) in petroleum products produce two major problems; they act as catalyst to speed autoxidation and gum formation; they combine with organosulfur compounds (thiols) to form insoluble salts (metal mercaptides). The copper mercaptides are particularly troublesome because they form gel-like deposits that can cause clogging of filters and fuel nozzles.

36. Metal reactivity is managed in fuel storage and transportation facilities by adding metal deactivators that can combine with and hold the metals in soluble organic compounds. Figure 3 shows the structure of N,N - disalicylidene propylenediamine, a heavy metal scavenging agent commonly used metal deactivating additives.

37. The effectiveness of any metal deactivator is directly related to the stability of the scavenging compound and its metal complexes and the degree of metal contamination. No data on long-term metal complex stabilities are available and no data have been developed on potential heavy metal contamination from storage and transfer operation.

38. It may be possible to extract metal complexes and metal deactivator agent from petroleum products in storage by caustic scrubbing and therefore renew the chelating or deactivating agents periodically. Existing patterns in fuel storage and distribution do not require long-term stability so no technology for cleaning fuel in storage currently exists. Technical development and testing will be required if metal deactivation additives are used in long-term fuel storage.



N, N′-disalicylidene-1,2-diaminopropane
(N,N′-disalicylidene propylenediamine)

Figure 3. Chemical structure of chelating agent used as a metal deactivator.

Pour Point Increase

39. In the heavy oils (crude and residual oils) and middle distillate, the ability to pump, flow, or pour the material can be severely affected by the growth of wax crystals as the oil cools. After waxes have separated, relatively high temperatures are required to remelt the solids.

40. To prevent an increase in pour point in crude or heavy fuel oils, materials classed as pour point depressants or cold flow improvers can be added that prevent the growth of wax crystals. These materials attach to the surface of nucleating crystals and retard crystal growth. The microcrystals, if they remain small and equidimensional, present fewer problems in pumpability and filtration.

41. Cold flow improvers are not generally used over long period of time; they are added during times when climatic conditions require their use. No data are available on their stability or eventual depletion in stored fuel or crude oil. If pour point depressants are employed in large quantity, long-term storage of fuel and crude oils, testing and evaluation will be necessary.

42. The feasibility of heating No. 6 residual oil is a function of the viscosity or state to which it is permitted to solidify. The most time efficient method of retrieval would be to keep the entire mass in the liquid state circulating within the reservoir. The duration of storage may make this an inefficient (energy) method when compared to the solidify/liquify process whereby the material is liquified at the time of extraction. Another factor to be considered is energy efficiency being dependent upon storage media, in which case surface storage will have a continuous heat loss the rate of which is a function of reservoir and external temperatures.

43. The solidification or formation of gel consistency residual No. 6 oil will cause unique problems in heating. The heating system, if installed at the bottom of the storage facility, will initially heat the oil to a fluid state, but the ability of the oil to convectively dissipate the heat energy is extremely limited. Agitation systems in conjunction with the heating system must be employed. The heating of the entire reservoir will be a time consuming effort.

Sludge Formation

44. Particulate material is almost always present in petroleum products and in most cases, if the material remains in suspension, it causes no problems in utilizing the fuel. However, there autoxidation or wax formation causes particulates to increase, clogging can become a problem.

45. Nitrogen-based surfactants have proved very useful in preventing settling and accumulation of sediment. One common material used in fuels is oleoyl amide. Salts of alkylbenzenesulfonic acid are also employed as dispersing agent in oils. All surfactants are long-chain polymers having both polar active and oil soluble groupings. The dispersant is consumed as it coats the surfaces of particles suspended in the oil and if no additional surfactant is added, dispersion in the oil will drop off and sediment formation will be accelerated.

46. Most dispersants appear to be stable to normal storage temperature. Dupont (Appendix A) has reported that its dispersant product, FOA-2, is "completely stable" for long periods at temperatures up to 150°F (65°C). All surface-active agents used with fuels may, if poorly managed, produce water-in-oil emulsions that are very difficult to break. If the treated oil product is agitated with water, especially acidic water, emulsification can occur. In general, the lower the pH the more stable the emulsion.

47 Dispersants suitable for use in long term may presently be available; but a testing program and research into management of treated products will be required to assure that complications due to emulsion formation and consumption of surfactant do not occur.

Bacterial Activity

48. Bacterial or microbial activity affects stored petroleum products by:

a. Direct attack on the petroleum hydrocarbons with the production of masses of bacterial cells that can produce clogging.

b. Microbial attack on organic fuel additives with the production of sediment.

c. Production of hydrogen sulfide in tank-bottom water with subsequent generation of corrosive organic sulfides.

d. Microbially moderated corrosion of iron in contact with tank-bottom water (Davis, 1967).

49. The direct utilization of hydrocarbon by bacteria normally occurs in water associated with the fuel. When the fuel and water mix together during loading or unloading masses of bacterial cells become entrained in the fuel and can clog fuel strainers. Microbial cells also can cause the formation of emulsions that can add further to fuel contamination. Some fuel additives can support the growth of bacteria more readily than the fuels themselves. Davis (1967) noted that the surfacant, phosphotidycholine (a jet-fuel additive) is a better source of carbon for bacteria than the fuel itself. When the material is used it must be protected by a bactericide.

50. Sulfate-reducing bacteria growing in water associated with fuel, especially kerosine jet fuel can produce elevated levels of corrosive organic sulfur compounds in the fuel. Stagnant sea water, because of its high sulfate content, can be particularly harmful to fuel.

51. Organic polymer coating on fuel tanks is also subjected to microbial attack. Some bacteria can use tank coatings as a sole carbon source. In other cases coatings appear to have suffered from attack by microbial metabolic products.

52. Bacterially-moderated corrosion can be severe in steel or concrete tanks. Zajic (1969) reviewed effects of bacteria in corrosion and cited these major microbial activities.

a. Formation of sulfuric acid and organic acids.

b. Depolarization of metal surfaces by oxidizing hydrogen.

c. Production of corrosive hydrogen sulfide.

Figure 4 shows the bacterially-moderated corrosion scheme postulated by Zajic (1969).

53. Bactericides have been widely used to control microbial effects in petroleum storage. Most of these compounds dissolve in the petroleum product but, move into any aqueous phases associated with the stored material. Many compounds have been found to have suitable antimicrobial activity. Diamines and polychlorinated phenolic compounds have been particularly useful. All of these compounds poison contacting water to inhibit microbial growth.

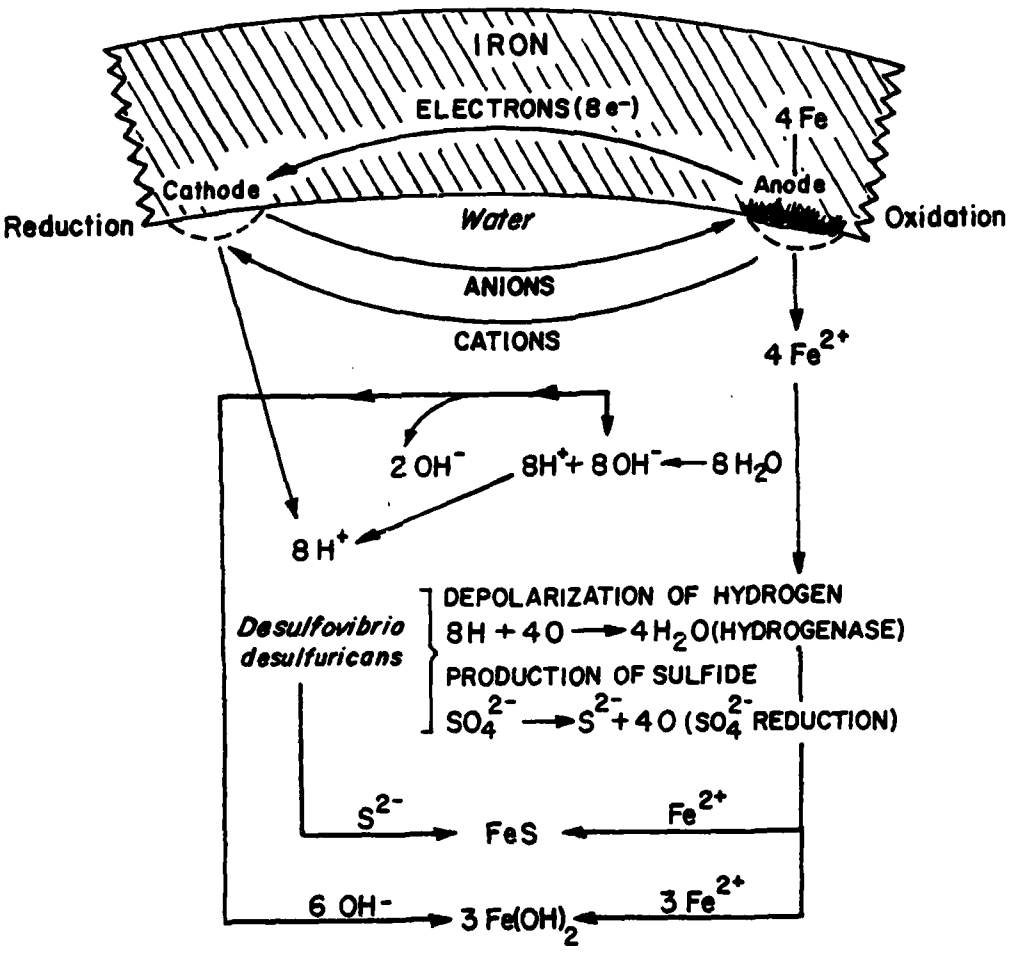


Figure 4. Schematic diagram showing reactions involved in bacterially moderated corrosion of iron.

54. No data are available in the literature on long-term stability of the bactericides. Generally these materials would be deactivated by absorption on particulates or oxidation. Testing of bactericides for use in long-term storage would be required.

Corrosion

55. Corrosion is the general term for degradation of metal parts due to chemical or electrochemical attack. Weak acids in petroleum may produce direct chemical attack or where water is present; a corrosion cell will form. Figure 5 shows a typical corrosion cell as postulated by Zajic (1969).

56. Additives have been prepared for stored oil products that limit corrosion by coating the sides of storage vessels or piping to isolate them from water, organic acids or hydrogen sulfide. These additives are primarily organic compounds with a strong affinity for metal surfaces. Anticorrosive additives can be lost by adsorption to surrounding surfaces, oxidation and bacterial degradation.

57. No data are available on long-term usefulness of anticorrosion additives. These materials would have to be tested for effectiveness and stability before their incorporation in storage planning.

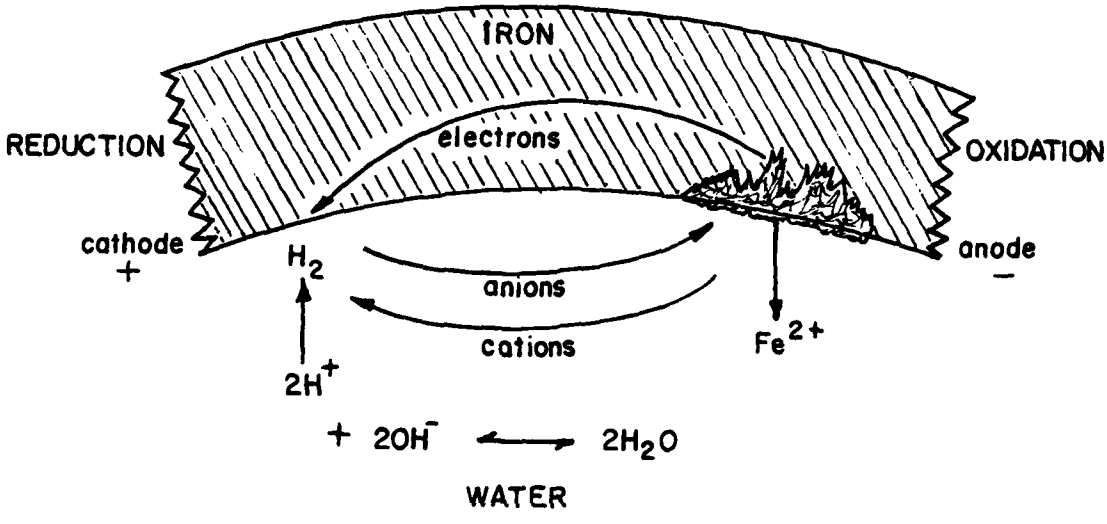


Figure 5. Schematic diagram showing reactions involved in corrosion of iron.

PART IV: SELECTED ADDITIVE EFFECTS

58. The following tables (4-7) list the specific additives recommended by the indicated distributors of petroleum product additives. The material presented represents a compilation of data from distributor literature and communication with manufacturer's representatives. A complete set of product descriptions and applications (Appendix A, parts 1 through 4) covers a multitude of applications and producer blends. Also included in Appendix A are price guidelines from two distributors. The general availability of prices was limited due to constant revisions or price list preparation by distributors. The list of contacts (Appendix B) is provided for acquisition of current costs.

Table 4

Treatment Rate for E. I. DuPont De Nemours and Co. Additives

	Product Pour Point	A/O	Metal Deact.	Pour Point Depressant*	Dispersant	Bactericide	Corros. Inhibitor
Crude Oil							
AO-35	-29°C	3-10 lbs					
DMD	-54°C		1/4-2 lbs				
Residual Oil							
Jet Fuel							
DMD	-18°C		1/4-2 lbs				
DCI-4A	-54°C						3-8 lbs
DCI-6A	-51°C						2-8 lbs
AO-22		3-10 lbs					

NOTE: Dosages in pounds per 1000 Bbls unless otherwise stated. A/O = Antioxidant. See Appendix A Part 1 for additional product listing and information.

* DuPont does not produce Pour Point Depressants.

Table 5

Treatment Rate for Ethyl Corporation Additives

	Product Pour Point	A/O	Metal Deact.	Pour Point Depressant	Dispersant	Bactericide	Corros. Inhibitor
Crude Oil							
Residual Oil							
Jet Fuel							
733	17°C	6-8					
735	36°C	6-8					
701	27°C	6-8					
PDA	14°C	NA					
PDA(O)	-2°C	NA					
MDA 80	-26°C		1-3				
MDA 50	-68°C		1-3				

NOTE: Dosages in pounds per 1000 Bbls unless otherwise stated. A/O = Antioxidant. NA = Not Applicable.

Table 6

Treatment Rate for Petrolite Additives

	Product Pour Point	A/O	Metal Deact.	Pour Point Depressant	Dispersant	Bactericide	Corros. Inhibitor
Crude Oil							
Tolad 31	-34°C			200-400 ppm			
XC-320	-28°C					30-500 ppm	
KI-16	-29°C		38 ppm add. per ppm Va.*				
Residual Fuel							
KI-16	-29°C		38 ppm add. per ppm Va.*				
Jet Fuel							
Tolad 37	-42°C			150-1500			
Tolad T-260	-40°C				10-20		
Tolad 245	-41°C						5-10 rust

NOTE: Dosages in pounds per 1000 Bbls unless otherwise stated. A/O = Antioxidant. Bactericide is used in industrial water system at storage facility.

* Va = Vanadium

Table 7

Treatment Rate for UOP Additives

	Product Pour Point	A/O	Metal Deact.	Pour Point Depressant	Dispersant	Bactericide	Corros. Inhibitor
Crude Oil							
Polyflo 100	< 65°F	2-20	--		2-20		--
Polyflo 130	< 10°F	2-20	--		2-20		4-20
Polyflo 140	<-30°F	2-20	--		2-20		--
Copper Deactivator AW50	-20°F	--	*		--		--
Unicor	-50°F	--	--		--		1-10
Unicor M	-35°F	--	--		--		1-5
Residual Oil							
Polyflo 100	< 65°F	2-10	--		2-10		--
Polyflo 130	< 10°F	2-10	--		2-10		2-10
Polyflo 140	<-30°F	2-10	--		2-10		--
Copper Deactivator AW50	-20°F	--	*		--		--
Unicor	-50°F	--	--		--		1-10
Unicor M	-35°F	--	--		--		1-5
Jet Fuel							
Polyflo 120	-70°F	1-10	--		--		--
Polyflo 121	-70°F	1-10	1-10		--		--
Polyflo 122	-15°F	1-10	1-10		1-10		1-20
UOP No. 5	< 0°F	1-10	--		--		--
UOP No. 12-P	-15°F	1-10	--		--		--
UOP No. 17-P	<-50°F	1-10	--		--		--
Copper Deactivator AW50	-20°F	--	1-4		--		--
Unicor PL	-30°F	--	--		--		1-10
Unicor J	-60°F	--	--		--		1-10
Unicor	-50°F	--	--		--		2-20
Unicor M	-35°F	--	--		--		1-10

NOTE: All dosages in pounds per 1000 bbls unless otherwise stated.
A/O = Antioxidant.
* Not practical.

PART V: EVALUATION

59. Long-term storage of petroleum distillates has been accomplished in the United States and various foreign countries. The successful storage of such materials for periods of up to 10 years indicated longer storage is possible. Such storage requires proper specification of products, product compatability, monitoring and use of additives which retard oxidation, sediment accumulation, biological activity, and polymerization.

60. Additives chemistry and variations in crude and petroleum product composition make generalizations about applications to long-term storage difficult. Many additives are appropriate for a general category of products, but may require actual laboratory testing to confirm capatability with specific products of mixtures of products.

61. Short-term usage of the additives in present storage facilities does not necessitate monitoring. Long-term storage with mixing, pumping, and heating adds additional variables whose effects cannot be predicted; therefore extensive testing and monitoring will be required. Petroleum products, additives, and handling techniques will continually modify the system and thereby interactions within the system.

62. Products additives that have been tested for short-term storage are available. Based on their usefulness in improving storage stability, it is advantageous to pursue a testing and evaluation program to see if products such as those listed in this reports (or modifications of these materials) would be effective in a long-term storage program.

PART VI: CONCLUSIONS AND RECOMMENDATIONS

63. Long-term (over 15 years duration) bulk storage of crude oil and petroleum products is a new operation and experience is limited. Crude oil has been held in storage for up to 10 years in Sweden; but this was live storage with crude being constantly added and removed. Finished products have rarely been stored for more than two years; six-month storage time is typical.

64. The use of any additives depends very strongly on the complete storage plan. If the stored material is a product destined for immediate use (such as kerosine or fuel oil), rather than a refinery feedstock (such as crude oil or naphtha) then any gum or emulsion formation is extremely detrimental. If the material is going to be refined, some introduction of additional impurities can be tolerated.

65. If the storage system calls for using rock-wall cavities, addition of anticorrosive agents may be necessary only when the material is pipelined out of storage.

66. Continual application of dispersants to fuel in storage may not be useful if the storage system has provisions for removing tank bottom sludges and cleaning the product being withdrawn. If heating and pumping of storage material is being considered, it should be noted that dispersants can cause emulsions when the petroleum and small amounts of water are mixed.

67. If the stored material is to be maintained at a uniform temperature, cold flow improvers may not be useful; but, provision may be made for adding these materials during emergency heating shutdowns or at the time of withdrawal (if pipeline temperatures are low).

68. Monitoring of the effectiveness and stability of any additions used will be a necessity in any storage program. The storage and volumes of material involved are so far beyond the scale of existing additive applications that testing and stability prediction systems now developed may not be dependable.

69. Experience to date with the additives reviewed in this report has shown that they are useful and stable in normal small-scale, short-duration (6 months) storage. There is no major reason that additive manufacturer's have discovered for not assuming the materials will be as effective in protecting petroleum products or feedstock for 10 to 20 years. If additives are to be employed, new testing procedures (such as new accelerated aging of petroleum

products tests) or modifications of existing accelerated testing procedures will be needed.

70. From the review of petroleum additives undertaken in this report it can be concluded that:

a. Many potentially useful petroleum additives exist and the selection of which types to employ depends on the complete storage plan.

b. Present experience and accelerated testing procedures are inadequate to predict the behavior of additives for the scale and time duration involved in a regional petroleum reserve, therefore any storage program must include a comprehensive monitoring program.

c. Experience with additives that are currently marketed is such that no new development of additives would seem to be necessary; but, extensive testing of additives and development of new testing procedures to duplicate long-term storage conditions may be required.

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APPENDIX A

PART 1

Dupont Corporation

OR-4828-D REV. 5-44

DUPONT
ESTABLISHED 1802

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
PETROLEUM LABORATORY
WILMINGTON, DELAWARE 19898

TELEPHONE
AREA CODE 609-299-5000
(Ext. 2638)

cc: A. J. Pahnke

March 28, 1980

Mr. Robert J. Larson
US AE-WES EE
P. O. Box 631
Vicksburg, MS 39180

Bob,

Find enclosed product bulletins as follows:

DCI-4A, corrosion inhibitor, recommended for jet fuel;
DCI-6A, corrosion inhibitor, recommended for ground fuels;
AO-35, antioxidant, recommended for jet fuel;
AO-22, antioxidant, recommended for gasoline;
FOA-3, antioxidant, recommended for distillate fuels; and
DMD, metal deactivator, recommended for any of the above fuels.

Our corrosion inhibitors are used at 1-4 lb/1000 bbl in gasoline and distillate fuels and at 3-8 lb/1000 bbl in jet fuel. Our antioxidants are used at about 3-10 lb/1000 bbl and DMD is used at ½-2 lb/1000 bbl. Additional details are in the product bulletins.

As I indicated during our telephone conversation, we do not market either pour point depressants or jet fuel anti-icers.

Please call me after you've reviewed this information. I'll be glad to provide samples and have our prices sent to you.

Very truly yours,

Perry Polss

Perry Polss, Supervisor
Petroleum Additives Division

PP/eaa
Enclosures

DUPONT

Petroleum Chemicals

PRODUCT SUMMARY

PETROLEUM ADDITIVES PRODUCT LISTING

ANTIKNOCK COMPOUNDS

PM Antiknock: A liquid antiknock compound, the active component of which is a physical mixture of tetraethyl lead and tetramethyl lead. Several mixtures are made by changing the molar percentages of the different lead alkyls. These mixtures are identified by the molar percentage of the tetramethyl lead which is present in the active ingredient.

Antiknock	Molar % TML
PM 10	10
PM 25	25
PM 50	50
PM 75	75

USE. As an antiknock agent for motor gasolines. CONTAINERS: Liter cans; 10- and 55-gal. drums; 3000-, 6000- and 9600-gal. tank cars.

Dilute* PM Antiknock: A liquid solution of a PM antiknock in a mixture of 70% xylene and 30% n-heptane. USE: For PM blending of gasolines used in laboratory engine testing. CONTAINERS: Liter cans.

TEL Aviation Antiknock: A liquid antiknock compound, the principal component of which is tetraethyl lead ($C_2H_5)_4Pb$. USE: As an antiknock agent for aviation gasolines. CONTAINERS: Liter cans; 10- and 55-gal. drums; 3000-, 6000-, and 9600-gal. tank cars.

TEL Motor Antiknock: A liquid antiknock compound, the principal component of which is tetraethyl lead ($C_2H_5)_4Pb$. USE: As an antiknock agent for motor gasolines. CONTAINERS: Liter cans; 10- and 55-gal. drums; 3000-, 6000-, and 9600-gal. tank cars.

Dilute* TEL Antiknock: A liquid solution of either TEL Motor Antiknock or TEL Aviation Antiknock in a mixture of 70% xylene and 30% n-heptane. USE: For TEL blending of gasolines used in laboratory engine testing. (The dilute TEL Antiknock made from TEL Aviation Antiknock is the approved reference material for ASTM Research and Motor Knock Test Methods.) CONTAINERS: Liter cans.

Tetramix® Antiknock: A liquid antiknock compound, the active component of which is a redistribution mixture of tetraethyl lead and tetramethyl lead. Several redistribution mixtures are made by changing the molar percentages of the different lead alkyls. These mixtures are identified by the molar percentage of the TML used in the reaction.

Antiknock	Molar % TML
Tetramix 25	25
Tetramix 50	50
Tetramix 75	75

USE: As an antiknock agent for motor gasolines. CONTAINERS: Liter cans; 10- and 55-gal. drums; 3000-, 6000-, and 9600-gal. tank cars.

Dilute* Tetramix® Antiknock: A liquid solution of a Tetramix Antiknock in a mixture of 70% xylene and 30% n-heptane. USE: For Tetramix blending of gasolines used in laboratory engine testing. CONTAINERS: Liter cans.

TML Antiknock: A liquid antiknock compound, the principal component of which is tetramethyl lead ($CH_3)_4Pb$. USE: As an antiknock agent for motor gasolines. CONTAINERS: Liter cans; 10- and 55-gal. drums; 3000-, 6000-, and 9600-gal. tank cars.

Dilute* TML Antiknock: A liquid solution of TML Antiknock in a mixture of 70% xylene and 30% n-heptane. USE: For TML blending of gasolines used in laboratory engine testing. CONTAINERS: Liter cans.

ANTIOXIDANTS

Antioxidant No. 22: N,N'-di-sec.-butyl-p-phenylenediamine containing no solvent. A mobile liquid readily soluble in gasoline in all proportions and at operating temperatures; Sp. Gr. 0.94. USE: To sweeten gasoline and retard the formation of gum and precipitation of antiknock compounds in gasoline. CONCENTRATION: 1 to 20 lb/M bbl. CONTAINERS: 55-gal. (425-lb.) steel drums, tank cars and tank trucks.

Antioxidant No. 23: A 50% by weight active ingredient, principally N,N'-di-isopropyl-p-phenylenediamine, in anhydrous methanol. Sp. Gr. 0.89. The product is readily soluble in gasoline at normal use concentrations. Aromatic gasolines or solvents can be used to prepare concentrated solutions. USE: For inhibiting the oxidation of gasolines, catalyzing the sweetening of sour blending stocks, and inhibiting the precipitation of antiknock compounds in gasoline. CONCENTRATION: 1 to 20 lb/M bbl. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Antioxidant No. 23 Concentrate: Principally N,N'-di-isopropyl-p-phenylenediamine. Reddish crystals; density at 157°F (57°C): 0.92. Aromatic gasolines or solvents can be used to prepare concentrated solutions. USE: For inhibiting the oxidation of gasolines, catalyzing the sweetening of sour blending stocks and inhibiting the precipitation of antiknock compounds in gasoline. CONCENTRATION: 1 to 15 lb/M bbl. CONTAINERS: Tank car and tank truck only.

*Dilute solutions are available in two mixtures to provide for greater accuracy when adding small volumes of the antiknock to gasolines for use in laboratory engine testing. (1) Gram Basis: 2 ml added to 400 ml of gasoline gives an elemental lead content of 2 grams of Pb per U.S. gallon. (2) Milliliter Basis: 2 ml added to 400 ml of gasoline gives the same elemental lead content as in 2 ml of TEL per U. S. gallon.

Antioxidant No. 29: 2,6-Di-tert-butyl-4-methyl phenol: A light colored, finely divided solid; non-coloring and readily soluble in oils; bulk density 0.61 g/cc. USE: In turbine, transformer and hydraulic oils, waxes and greases to retard oxidation, and in gasoline to reduce the formation of gum and precipitation of antiknock compounds. CONCENTRATION: 2 to 20 lb/M bbl. CONTAINERS: 20-gal. (100-lb.) fiber drums.

Antioxidant No. 30: 100% alkylated phenols, principal active ingredient—2,4-dimethyl-6-tert-butylphenol (97% minimum). A straw-colored liquid, readily soluble in gasolines and oils. Sp. Gr. 0.96. USE: In turbine, transformer, and hydraulic oils, waxes and greases to retard oxidation, and in gasolines to reduce gum formation and precipitation of antiknock compounds. CONCENTRATION: 1 to 10 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

Antioxidant No. 31: 100% alkylated phenols, principally 2,4-dimethyl-6-tert-butylphenol (72% minimum). A yellow-colored liquid, readily soluble in gasolines and oils. Sp. Gr. 0.97. USE: In turbine, transformer, and hydraulic oils, waxes, and greases to retard oxidation, and in gasolines to reduce gum formation and precipitation of antiknock compounds. CONCENTRATION: 1 to 10 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

Antioxidant No. 33: 100% alkylated phenols, principally 2,4-di-tert-butylphenol. An amber liquid readily soluble in gasolines and oils. Sp. Gr. 0.93. USE: In turbine, transformer and hydraulic oils, waxes, and greases to retard oxidation, and in gasolines to reduce gum formation and precipitation of antiknock compounds. CONCENTRATION: 1 to 10 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

Antioxidant No. 35: 100% alkylated phenols, principally butylated ethyl phenols and butylated methyl and dimethylphenols. An amber liquid readily soluble in gasolines and oils. Sp. Gr. 0.96. USE: In turbine, transformer, and hydraulic oils, waxes, and greases to retard oxidation, and in gasolines to reduce gum formation and precipitation of antiknock compounds. CONCENTRATION: 1 to 10 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

DYES

Hydrocarbon soluble dyes for imparting distinctive colors to gasoline and other petroleum products. Available in flake, powder and liquid form.

Oil Blue A: Essentially 1,4-di(isopropylamino)-anthraquinone. Solvent Blue 36 Color Index 61551. Dry form in flakes only.

Oil Blue B Liquid: Anthraquinone dye.

Oil Bronze: A blend of oil red and oil orange dyes. Dry form in both powder and flakes.

Oil Bronze Liquid: Azo dye.

Oil Bronze Y Liquid: Azo dye.

Oil Bronze No. 2 Liquid: Azo dye.

Oil Green Liquid: Azo dye.

Oil Orange: Essentially phenylazo-2-naphthol. Solvent Yellow 14 Color Index 12055. Dry form in both powder and flakes.

Oil Orange Liquid: Azo dye.

Oil Orange B Liquid: Azo dye.

Oil Orange Y Liquid: Derivative of azoresorcinol dye.

Oil Orange YR Liquid: Derivative of azoresorcinol and azobenzene-azonaphthol dye.

Oil Purple Liquid: Azo dye.

Oil Red: Essentially methyl derivatives of azobenzene-4-azo-2-naphthol. Solvent Red 24 Color Index 26105. Dry form in both powder and flakes.

Oil Red A: Essentially methyl derivatives of azobenzene 4-azo-2-naphthol. Slightly stronger and bluer than Oil Red. Dry form in both powder and flakes.

Oil Red B Liquid: Azo dye.

Oil Red BT Liquid: Azo dye.

Oil Red G Liquid: Azo dye.

Oil Yellow Liquid: Azo dye.

Oil Yellow NB: Essentially p-diethylaminoazobenzene. Dry form in pellets.

Oil Color IA, Oil Color IAR (Identification Agents): Proprietary. Used for identification purposes. Dry powder colors: blue and red, respectively.

CONTAINERS: Dry forms: 100-lb. (net) fiber drums. Liquid form: 240-lb. (net) 30-gal. steel drums, tank cars and tank trucks.

FUEL OIL ADDITIVES

Fuel Oil Additive No. 2: 50% methacrylate polymer and 50% kerosine. A viscous, amber, ashless liquid. Miscible in No. 2 fuel oil in all proportions. Sp. Gr. 0.89. USE: To retard the formation of insoluble residues in heating oils, diesel fuels and similar products. Also functions as a dispersant to keep any sludge which is already present, or which may form, in small particles which will pass through filters and screens. CONCENTRATION: 10 to 30 lb/M bbl. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additive No. 3: A complex amine, clear, straw-colored liquid. Sp. Gr. 0.86. USE: An ashless antioxidant and color stabilizer for burner and diesel fuels. Broader properties obtained by blending with metal deactivator or Fuel Oil Additive No. 2. CONCENTRATION: 1 to 20 lb/M bbl. CONTAINERS: 55-gal. (386-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additives No. 11 and No. 12: Combinations of FOA-2, FOA-3 and DMD. Light amber, ashless liquid. Miscible in fuel oil in all proportions. Sp. Gr. 0.88-0.89. USE: For fuel and diesel oils to impart antioxidant and color stabilizing properties along with dispersant and metal deactivation. FOA-12 has greater dispersancy than FOA-11. Similarly, FOA-11 has better antioxidant properties than FOA-12. CONCENTRATION: 5 to 30 lb/M bbl. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additive No. 14: Mixture of polymer and organic amines. Ashless, light amber liquid. Sp. Gr. 0.87. Miscible in fuel oil in all proportions. USE: For fuel and diesel oils to impart antioxidant, dispersant properties, metal deactivation, and color stability while improving the water emulsion and haze resistance of burner and diesel fuel oils.

CONCENTRATION: 5 to 30 lb/M bbl. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additive No. 15: Mixture of polymers and organic amines. Amber colored liquid. Miscible in fuel oils. Sp. Gr. 0.90. USE: Multifunctional additive to impart to fuel oils rust inhibition, dispersancy, antioxidant properties, color stability and metal deactivation. CONCENTRATION: 5 to 30 lb/M bbl. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additives No. 208 and No. 212: A mixture of Fuel Oil Additive No. 2 and metal deactivator. USE: Same as Fuel Oil Additive No. 2. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additive No. 310: Amber, ashless liquid. Miscible in all proportions. Sp. Gr. 0.86. USE: For fuel and diesel oils. Imparts antioxidant and color stabilizing properties along with metal deactivation. CONCENTRATION: 1 to 20 lb/M bbl. CONTAINERS: 55-gal. (386-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additive No. 405: Amber, ashless liquid. Miscible in all proportions. Sp. Gr. 0.91. USE: For fuel and diesel oils. Imparts antioxidant and color stabilizing properties, corrosion inhibition and metal deactivation. CONCENTRATION: 2 to 8 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

Fuel Oil Additive No. 937: A dehaze agent for breaking water/oil emulsions. Sp. Gr. 0.85. USE: For fuel and diesel oils. CONCENTRATION: 1 to 3 lb/M bbl. CONTAINERS: 55-gal. (390-lb.) steel drums.

MHFA-1 Marine Heavy Fuel Oil Additive No. 1: An ashless polymeric combination of several completely organic compounds in kerosine. A clear, yellow liquid. Sp. Gr. 0.86. USE: To inhibit sludge formation and remove sludge deposits which cause filter clogging, fouled heat exchangers, etc., thereby providing fewer operating interruptions and reduced maintenance costs. Used also in diesel fuels to avoid injector sticking and filter plugging problems. CONCENTRATION: 0.5 to 5.0 pints/M gallons of fuel. CONTAINERS: 55-gal. (386-lb.) steel drums.

Stadis® 125 Conductivity Improver: A nonmetallic, low viscosity, clear amber liquid. Sp. Gr. 0.90. USE: Improves conductivity to reduce electrostatic hazards during transfers of distillate fuels without affecting fuel stability or water contact properties. CONCENTRATION: 0.5 to 5.0 lb/M bbl. results in a recommended conductivity of 50 c.u. or more. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Stadis® 450 Conductivity Improver: A nonmetallic, low viscosity, clear amber liquid. Sp. Gr. 0.90. USE: Improves conductivity to reduce electrostatic hazards during transfers of distillate and jet fuels without affecting fuel stability or water contact properties. CONCENTRATION: 0.1 to 1.0 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

GASOLINE ADDITIVES, MULTIFUNCTIONAL

DMA-4 (Multifunctional Additive): An 80 weight percent solution of alkylaminoalkylphosphate in kerosine. Clear, nearly colorless, light viscosity liquid. Sp. Gr. 0.92. USE: An additive for gasolines to eliminate carburetor icing, provide carburetor detergency, prevent rusting, control exhaust emission levels and provide better emission system operation. CONCENTRATION: 5.0 to 30 lb/M bbl. Antirust properties can be obtained with concentration as low as 0.5 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

DMA-4A (Multifunctional Additive): Same active ingredient as DMA-4, but contains 20% methanol solvent rather than 20% kerosine used in DMA-4. Provides excellent low-temperature handling properties and is compatible with antipre-ignition additives. Clear, nearly colorless, light viscosity liquid. Typical Sp. Gr. 0.92. CONCENTRATION: Same as DMA-4. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

DMA-50 (Non-Phosphorus Multifunctional Additive): Clear, amber liquid. Typical Sp. Gr. 0.91. USE: In gasoline where carburetor detergency and emissions control are desired benefits. Antirust and some carburetor anti-icing benefits are also obtained. CONCENTRATION: 5 to 12 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

DMA-54 (Non-Phosphorus Multifunctional Additive Containing An Antirust Additive): In addition to detergency and rust protection, it provides carburetor icing protection, fuel line freeze protection and aids in controlling exhaust emissions. Clear amber liquid. Typical Sp. Gr. 0.92. CONCENTRATION: 5 to 12 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

DMA-55 and DMA-56 (Non-Phosphorus Multifunctional Additives Containing An Antirust Additive): Clear amber liquid. Sp. Gr. 0.91. USE: Imparts carburetor icing protection, fuel line freeze protection, detergency, rust protection and aids in controlling exhaust emissions. CONCENTRATION: 5 to 10 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

DMA-115 (Multifunctional Additive): A polymer plus an amine-neutralized phosphate provides carburetor clean-up, keep-clean detergency, rust protection, emission control, and icing stall protection. Sp. Gr. 0.90. Recommended dosage is 107.5 lb/M bbl. CONTAINERS: 55-gal. (410-lb.) steel drums, tank cars and tank trucks.

LUBRICATING OIL AND GREASE ADDITIVES

Lube Oil Additive 565: A light neutral oil solution of methacrylate polymers in a viscous, ashless, liquid form completely miscible in oil in all proportions. Possesses detergent properties and viscosity improving ability. USE: A dispersant in crankcase oils, particularly under low duty or low engine temperature operation. CONCENTRATION: Normal range, 2.0 to 3.0 weight percent; wide range, 1.0 to 6.0 weight percent. CONTAINERS: 55-gal. (397-lb.) steel drums, tank cars and tank trucks.

Ortholeum® 162 Lubricant Assistant: Light brown viscous liquid; freezing point about 53°F. Sp. Gr. 0.99. Miscible with oil in all proportions. USE: In oils to improve film strength and wear reduction and to impart mild rust preventative properties. CONCENTRATION: 0.5 to 5.0 weight percent. CONTAINERS: 55-gal. (452-lb.) steel drums.

Ortholeum® 300 Grease Stabilizer: A mixture of complex aromatic amines which provides a combination of antioxidant and metal deactivator. It is a tan to brown colored, flaked product. USE: As a stabilizer for greases. CONCENTRATION: 0.1 to 1.0% by weight. CONTAINERS: 51-gal. (175-lb.) fiber drums.

Ortholeum® 308 Stabilizer: 1,4-dihydroxyanthraquinone. A brick-red solid. USE: As a metal deactivator in both synthetic and mineral base lubricants when used in conjunction with other additives. CONTAINERS: 30-gal. (100-lb.) fiber drums.

Ortholeum® 535 Lubricant Assistant: A clear pale yellow viscous liquid. Typical Sp. Gr. 0.95. USE: An ashless additive to impart antirust, antiwear and mild extreme pressure properties to greases, industrial oils, hydraulic oils and metal working fluids. CONCENTRATION: 0.05 to 1.0% by weight, depending upon application. CONTAINERS: 55-gal. (430-lb.) steel drums.

Ortholeum® 2004, 2010, 2035, and 2052 V. I. Improver: Solid ethylene/propylene polymers. USE: As viscosity index improvers. CONCENTRATION: Range is 6 to 12% by weight, depending upon application. CONTAINERS: 75-lb. bales wrapped with 6.0 mil polyethylene.

METAL DEACTIVATORS

Metal Deactivator: A 75% solution of active ingredient in an aromatic solvent. The active ingredient is principally N,N'-disalicylidene-1,2-propanediamine. A clear, amber liquid. Sp. Gr. 1.08. USE: For improving storage and color stability of petroleum distillates containing dissolved copper. It is particularly useful as an adjunct to Gasoline Antioxidants and Fuel Oil Additive No. 2. CONCENTRATION: Varies widely with application. CONTAINERS: 30-gal. (250-lb. and 55-gal. (483-lb.) steel drums, tank cars and tank trucks.

Metal Deactivator No. 2: A 50% solution of the same active ingredient as in Metal Deactivator, but having better low temperature properties. Sp. Gr. 0.99. USE: Same as Metal Deactivator. CONTAINERS: 30-gal. (247-lb.) and 55-gal. (452-lb.) steel drums, tank cars and tank trucks.

Metal Suppressor: An amber colored liquid, 50% alkyl acid salts of a complex organic amine, 50% solvent. USE: Counteracts the pro-oxidant effect of copper or copper alloys and thereby increases storage stability of gasoline and fuel oil exposed to such surfaces. CONCENTRATION: In gasolines, 0.5 to 4.0 lb/M bbl. In electrical oils and industrial lubricants, up to the solubility of the additive. CONTAINERS: 55-gal. (430-lb.) steel drums.

SPECIAL ADDITIVES

Ocenol® 2 Antifoam Additive: Clear, colorless liquid with typical fatty alcohol odor; Sp. Gr. 0.85. USE: Effective antifoaming agents in petroleum and organic bases such as mono- and diethanolamines. CONCENTRATION: Varies widely with the application. CONTAINERS: 55-gal. (386-lb.) steel drums.

AFA-1: 80% alkylaminoalkyl phosphate, 20% kerosine. Clear, light amber slightly viscous liquid; typical Sp. Gr. 0.93. CONCENTRATION: 1 to 20 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

DCI-3® Process Corrosion Inhibitor: A clear, nearly colorless liquid of light viscosity; typical Sp. Gr. 0.84. USE: To control corrosion of petroleum refinery processing units in the presence of hydrocarbons containing wet hydrogen sulfide. CONCENTRATION: 1 to 5 lb/M bbl. CONTAINERS: 55-gal. (386-lb. steel drums, tank cars and tank trucks.

DCI-4A: A nonphosphorus corrosion inhibitor for aviation and motor gasolines, jet fuels and other distillate fuels. A clear, amber liquid with typical Sp. Gr. of 0.94. CONCENTRATION: 1 to 8 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

DCI-6: A nonphosphorus corrosion inhibitor for motor gasolines and distillate fuels. A clear, amber liquid. Sp. Gr. 0.95. CONCENTRATION: 1 to 10 lb/M bbl. CONTAINERS: 55-gal. (419-lb. steel drums, tank cars and tank trucks.

DCI-6A: A nonphosphorus corrosion inhibitor for motor gasoline and distillate fuels. Amber liquid. Sp. Gr. 0.93. CONCENTRATION: 1 to 10 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

Rust Preventative No. 2: 80% solution in kerosine of an alkylaminoalkylphosphate. A straw colored liquid. Sp. Gr. 0.93. USE: As an antirust agent in petroleum distillates at concentrations up to 3 lb/M bbl. CONTAINERS: 55-gal. (419-lb.) steel drums, tank cars and tank trucks.

DUPONT

Petroleum Chemicals

FOR-2

DU PONT FUEL OIL ADDITIVE No. 2

INTRODUCTION

Du Pont Fuel Oil Additive No. 2 was designed specifically to improve the performance qualities of fuel oils. This product is an ashless non-metal-containing polymer and it improves the stability and serviceability of fuels by reducing markedly the formation of insoluble residues and sludges. It also serves to keep insoluble material which may be present in the fuel in a finely divided, well dispersed and harmless state. These qualities of Du Pont FOA-2 result in tangible benefits to the producers and consumers of fuel oils because they mean more trouble-free operation of fuel handling and burning equipment, lower maintenance costs, improved equipment performance and greater consumer satisfaction.

Du Pont FOA-2 has been used with outstanding success in home and industrial heating oils, diesel engine fuels--particularly those used by the railroads-- and in the heavy No. 5, No. 6 and Bunker C fuels. In these applications FOA-2 has not only been effective in overcoming problems due to sludge and insoluble residues, but has also given additional benefits such as minimizing incompatibility problems when fuels are mixed, reducing the sticking of diesel engine injectors and reducing deposits on oil burner nozzles and electrical system controls. With the heavy or residual fuels which contain appreciable amounts of impurities and insoluble matter, this additive has been remarkably effective in preventing filter-plugging and maintaining fuel-system cleanliness. It also has been valuable in removing sludge deposits from tanks used for storing heavy fuel.

Du Pont Fuel Oil Additive No. 2 is a product offering advantages which benefit both the producers and the consumers of distillate and residual fuels.

COMPOSITION AND PROPERTIES

Du Pont Fuel Oil Additive No. 2 is a viscous, light-amber liquid composed of 50 % of an active ingredient in kerosine. The active ingredient is a long-chain polymer of several completely organic compounds. They are combined in carefully tested proportions to effect the optimum balance between polar-active and oil-soluble groupings. The molecule is quite large and varies in size with an average molecular weight of approximately 280,000. Typical physical properties of Du Pont FOA-2 are as follows:

Color, ASTM D 1500	2-1/2 ± 1/2
Density, ASTM D 287	
g/ml @ 60F	0.89
pounds per gallon @ 60F	7.4
Ash, Wt. %, ASTM D 482	0.00
Basic Nitrogen wt %	0.4
Flash Point	
Pensky - Martens Closed Tester, ASTM D 93	135F (57.2 C)
Tag Closed Tester, ASTM D 56	125F (51.7 C)
Tag Open - Cup, ASTM D 1310	165F (73.9 C)
Cleveland Open Cup, ASTM D 92	170F (76.7 C)
Fire Point, F	
Cleveland Open Cup, ASTM D 92	175F (79.5 C)
Pour Point, F, ASTM D 97	Below -20F (-28.9 C)
Neutralization Number by Titration, ASTM D 664	
Acid Number (mg KOH/g sample)	0.2
Base Number (Eqvt. to mg KOH/g sample)	13.8
Solubility	
in Hydrocarbons	Completely Miscible
in Water, wt %	Less than 0.01

Viscosity, ASTM D 445	SUS	cs
@ 0 F (-17.8 C)	27,000	8,000
@ 32F (0 C)	11,100	2,400
@ 77F (25.0 C)	3,150	680
@ 100F (37.8 C)	1,855	400
@ 210F (98.9 C)	350	75

- Viscosity - Reduction by Dilution

Dilution of Du Pont Fuel Oil Additive No. 2 with distillate fuels or aromatic solvents will greatly lower the viscosity. The amount of the viscosity reduction by dilution with kerosine is shown in the following Table.

VISCOSITY REDUCTION BY KEROSINE DILUTION

FOA-2 Wt %	Kerosine Wt %	Viscosity @ 100 F cs	SUS
100	0	400	1854
75	25	132	612
50	50	34	159
25	75	8.4	53.5
0	100	1.385	-

- Thermal Stability

At normal use concentrations in fuel oils Du Pont FOA-2 has excellent thermal stability and can withstand temperatures of 200 F for prolonged periods.

Laboratory tests indicate that the additive itself is completely stable for long periods at temperatures up to 150 F. It can be subjected to temperatures up to 400 F for half an hour without any loss in effectiveness. At 500 F, which is above the initial boiling point of the kerosine solvent, a portion of the solvent will be distilled off and the active ingredient will start to depolymerize into monomers. At approximately 800 F, the product decomposes and volatilizes.

- Emulsification Properties

Extensive commercial use of Du Pont Fuel Oil Additive No. 2 has demonstrated that no emulsification problems will be encountered under normal conditions. However, in common with all surface-active agents, the additive, when subjected to unusually severe agitation with water, tends to form water-in-oil emulsions which break slowly. This is evident in many emulsification-tests in the laboratory.

The pH of the water has a large effect on emulsification properties. For example, in a laboratory test similar to the water reaction test of Method 3251, Fed. Test Spec. VV-L-791a, a fuel containing FOA-2 at a concentration of 20 pounds per 1,000 barrels gave the following results:

pH of Water Phase		Minutes for Separation
9	Alkaline	Less than 5
8		Less than 5
7	Neutral	Less than 5
6		9
5		20
4	Acid	50
3		75

The tendency toward emulsification is negligible when the water is neutral or slightly alkaline which is the usual field service condition. In the laboratory, the water used for emulsification-tests, even though distilled, is often acidic due to dissolved carbon dioxide. This condition can lead to unrealistic assumptions concerning "field" performance of fuels containing FOA-2.

USE-CONCENTRATION

The quantity of additive required for good results has been found to range from 5 to 60 lb/1000 bbl (approximately 17 to 204 ppm) depending on the fuel in which it is used. Normal dosage ranges from 10 to 30 lb/1000 bbl (approximately 34 to 102 ppm).

ADDITION OF DU PONT FUEL OIL ADDITIVE NO. 2

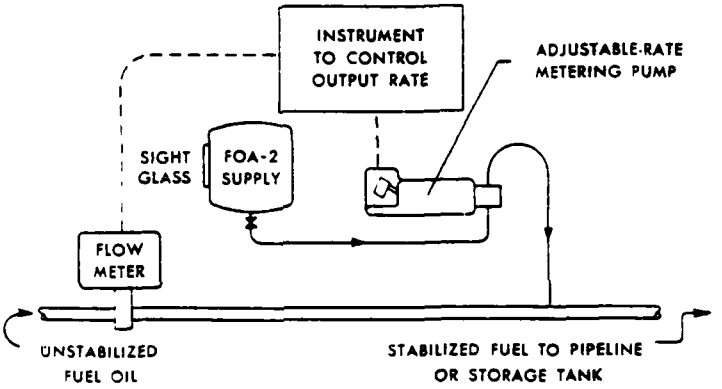
- Point of Addition

Maximum benefits from Du Pont Fuel Oil Additive No. 2 are obtained when it is added to fuels before they have aged appreciably. The addition should be made as soon as possible after any entrained water that is present in the fuel has had an opportunity to settle.

- Methods of Addition

The preferred method of addition is continuous injection of the additive to fuel oil in the proper ratio to the fuel by means of metering pumps. (See diagram below.) Control of the output rate of a metering pump, to maintain the desired ratio of additive flow, is usually obtained either by manual adjustments on the pump, or automatically through instruments. An automatic setup, often described as "flow-proportioning", includes a flowmeter on the oil pipeline, to which a control instrument responds with signals to a device at the pump to change its output. Alternate devices available include variable-speed drives, stroke-length adjusters, and timers linked with a solenoid clutch or an appropriate 3-way valve.

CONTINUOUS METHOD FOR ADDING FOA-2



NOTE: Automatic, flow-proportioning control system is optional, but recommended if fuel oil flows are variable.

Another method of adding FOA-2 is the batch method which is particularly suited to treating small quantities of fuel oil.

- Handling in Cold Weather

Regardless of which of these addition methods is used, when the additive is cold its viscosity may be too high for effective transfer and metering. To overcome this obstacle the product can be handled in a heated enclosure or in equipment provided with heating elements. Or, stock solutions of appropriate viscosity can be prepared by diluting Du Pont Fuel Oil Additive No. 2 with fuel oil or other suitable solvents. These stock solutions can then be added to the fuel oil by any of the suggested procedures.

Under some conditions it may also be advantageous to employ stock solutions when small quantities of the additive are handled.

More detailed information on these addition methods and handling techniques can be obtained from your Du Pont representative.

PERFORMANCE

- Insoluble Residue Formation in Fuels

Although the problem of fuel oil instability has been recognized for many years, little is known about the actual mechanism of insoluble residue formation. The deterioration of cracked fuels is believed generally to be associated with oxidation and the formation of free radicals. Oxidation occurs first, and is followed by polymerizations of the polar or non-hydrocarbon constituents of the fuel. When these polymerizations reach a certain point, the products are no longer soluble and precipitate from the fuel. Various investigators have shown that the polar compounds are directly connected with instability. Some research workers have removed the polar compounds and thereby stabilized certain fuels, while others. conversely, have promoted insoluble residue formation by adding to fuels selected sulfur and nitrogen-containing compouds. The concentration of oxygen, nitrogen and sulfur in insoluble residues is shown in the following Table, and compared with the typical amount of these elements in fuel oils.

ANALYSES OF INSOLUBLE RESIDUES OF NO. 2 HEATING OILS

Element	Percent by Weight In Fuel	In Residue
Carbon	83-86	50-85
Hydrogen	12-15	5-10
Sulfur	0.1-2.3	1-8
Nitrogen	0.002-0.4	0.5-6
Oxygen	0.03-1.0	6-30
Ash	0.01-0.10	6-20

In the past, some investigators have considered soluble gum as a precursor of insoluble residues and have postulated that, as the molecular weight has increased, solubility would decrease. However, thorough investigations of numerous distillate fuels of many types have never shown any relationship between the formation of soluble gum and insoluble residues. It is generally conceded that soluble gums have not been proved to have any relationship to commerical-use problems of distillate fuels.

- Theory of Additive Performance

Du Pont FOA-2 is a high molecular weight polymer that combines active polar and oil-soluble groupings in a carefully balanced relationship. The additive functions by reacting with non-hydrocarbon constituents of the fuel. In this way, it

prevents or retards the formation of insoluble residue by preventing the continued polymerization of these groups. The long chain, oil-soluble portion of the molecule protects the polar constituent from further reaction and solubilizes the total compounds. In instances of some residue formation occurring, the additive prevents agglomerations and maintains dispersion. The careful balance and relationship between the groupings of the polymer prevent the phenomena of "additive slugging" wherein an additive reacts with sufficient insoluble residue to be pulled out of solution and actually increase the amount of insoluble residue.

- 110 F Storage

The stabilizing effect of Du Pont FOA-2 can be determined in the laboratory by means of mildly accelerated storage tests. A temperature of 110 F maintained for 12 weeks has been found to correlate with approximately one year of bulk storage in the field in drums or tanks. The insoluble residues formed in the fuel during storage are determined by filtration. FOA-2 in these tests, as in field performance, consistently exhibits an ability to retard or reduce the insoluble residue formation, and to produce fuels which even after long storage are in good condition. A typical set of results on one fuel are shown in the table below.

No set level of insoluble residue can be considered as a positive indication that the fuel will be unsuitable for customer use. Many refiners, however, have established an upper limit on insoluble residue of 2 mg, 100 ml.

EFFECT OF FOA-2 ON S ORAGE STABILITY OF A NO. 2 FUEL OIL BLEND

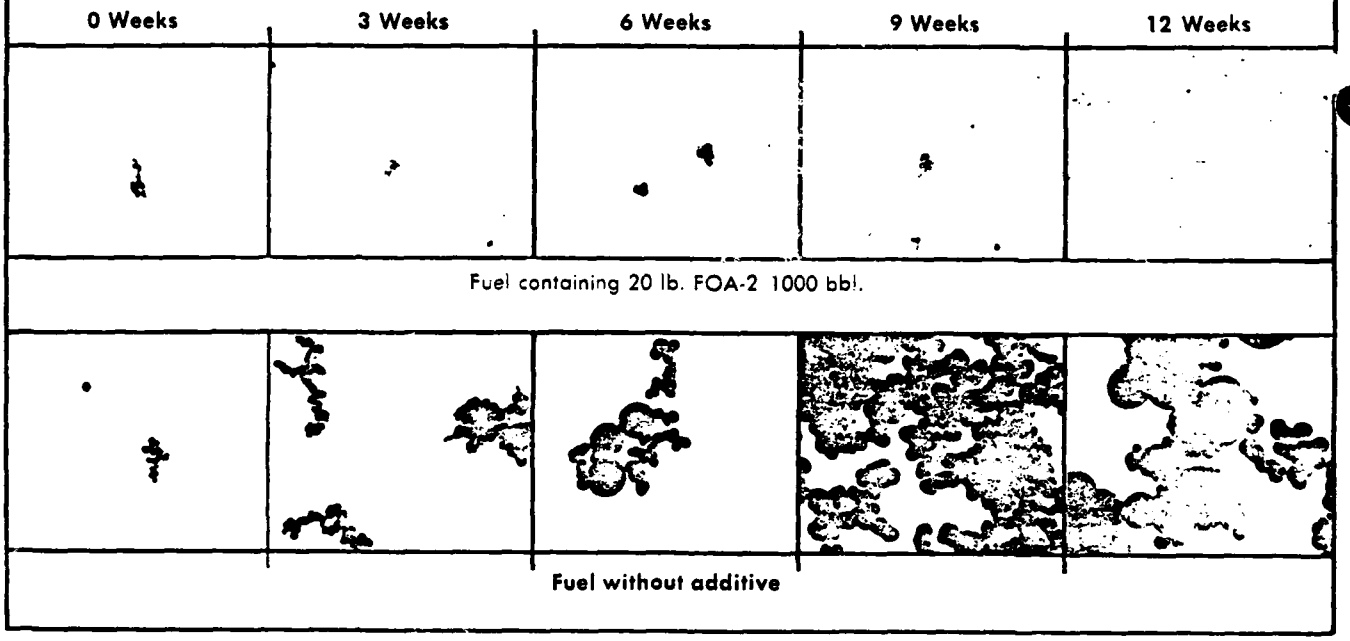
	FOA-2 Concentration in lb/1000 bbl	Weeks Aged @ 110 F 0	3	6	9	12
Insoluble Residue	None	0.5	1.7	2.1	2.9	5.7
mg /100 ml	15	0.5	0.9	1.5	1.2	3.8
	30	0.5	0.9	1.2	1.0	0.8
Visible Sediment	None	Nil	Sl.Sed.	Sl.Sed.	Sed.	Sed.
	15	Nil	Nil	Nil	Sl.Sed.	Sed.
	30	Nil	Nil	Nil	Nil	Nil
ASTM Color	None	3.5	3.5	4.0	L4.5	5.0
	15	3.5	3.5	4.0	L4.5	5.0
	30	3.5	4.0	L4.5	L5.0	5.0

• Electron Microscope

Du Pont Fuel Oil Additive No. 2 has the ability to prevent agglomeration of residue particles and keep these particles dispersed throughout the liquid and in small size so that they will pass through fine orifices or screen openings. The electron microscope is particularly suitable for studying the shape and size of residue particles from a fuel, and to reveal changes in them as the fuel is progressively aged. Some typical electron photomicrographs, obtained from a fuel aged with and without FOA-2 are shown in Figure 1.

FIGURE 1

FOA-2 MINIMIZES THE SIZE OF RESIDUE PARTICLES FORMED IN FUEL IN 110 F STORAGE



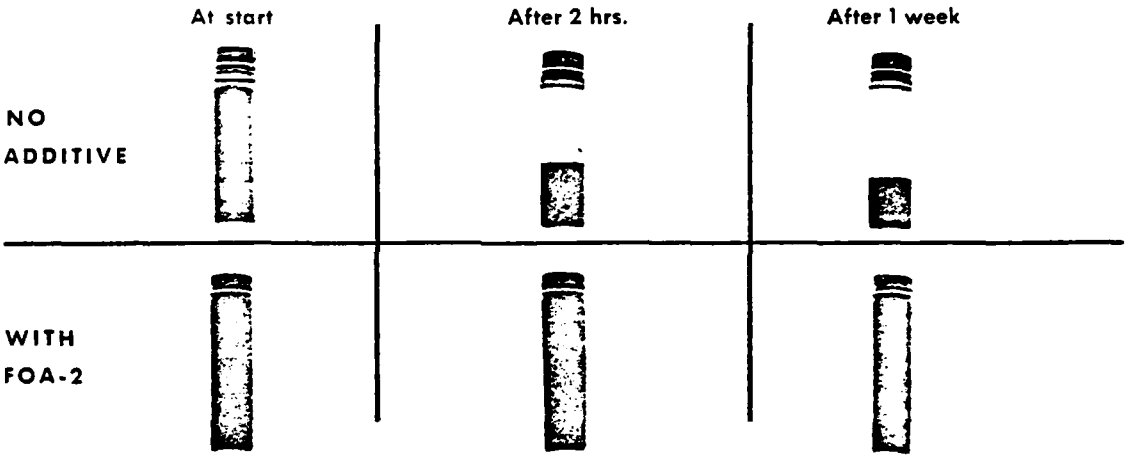
"SCALE" 0 (MICRONS) 5

- Carbon Dispersancy Test

The dispersancy power of Du Pont FOA-2 is also shown by a carbon dispersancy test in which carbon black is suspended in kerosine. Carbon black is similar to fuel oil residues in that it contains polar oxygen and sulfur groups, and the particle size is in the same micron range. As with fuel oil sludge, the carbon black will be suspended by FOA-2 for long periods in the hydrocarbon. An example of this is shown in Figure 2.

FIGURE 2

FOA-2 SUSPENDS CARBON BLACK IN KEROSINE



- Accelerated Tests

Producers and consumers often employ laboratory tests for predicting the storage stability characteristics of their fuels. Due to time limitations imposed by modern shipping and distribution schedules, these tests should not require more than 24 hours, and should be capable of predicting the behavior of fuels for varying periods of time up to several years.

Investigators have accelerated the aging of fuels, using numerous methods such as heating at elevated temperatures, exposure to light, and contact with oxygen. In addition, various metals have been utilized to simulate contacts to which fuels might normally be subjected in the field. The result has been the very large number of accelerated test techniques in use today. These tests are useful and serve a purpose, but are usually quite specific. The accelerated tests can be correlated for fuels produced from constant crude oil sources, processing

techniques and additive types. Under such conditions, they afford a norm of quality. Unfortunately, the correlation with field problems must be redeveloped if the processing method or the additive type changes.

Many of the elevated temperature tests have been referred to in connection with field problems associated with elevated temperatures such as nozzle-fouling and injector-sticking. These tests are useful in that connection if they are run after a period of storage at lower temperature--such as 110 F-- to simulate actual field conditions.

Over 15 years' commercial experience has proved that Du Pont FOA-2 gives outstanding performance in actual field use.

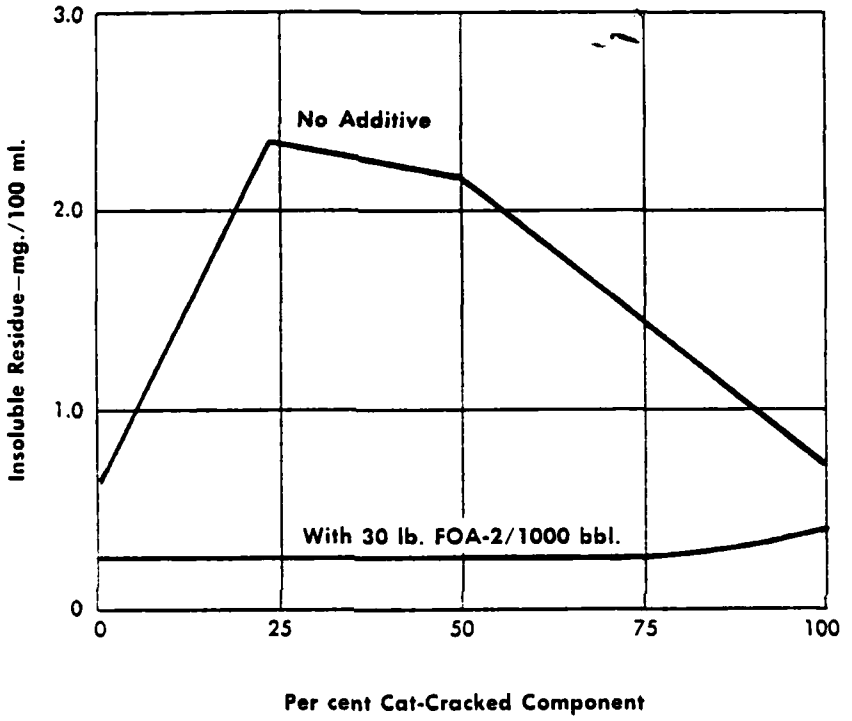
- Incompatibility

In the distribution and use of distillate fuels, it is almost impossible to keep one particular fuel oil stock completely segregated from all others. Somewhere, either in the refinery tanks themselves, during pipeline shipment and distributors' handling, or finally in the customers' own fuel tanks, some mixing or blending with other fuels occurs. Under these conditions many fuel oils, which by themselves will remain stable in storage for long periods will, when mixed with other fuels, produce gummy or insoluble deposits which give trouble in use. This characteristic of fuels has been designated as incompatibility. It is believed to be due largely to a solubility effect and partly to a synergistic effect of harmful constituents present in the different fuels. Several comprehensive investigations of two component blends of fuel oils have indicated incompatibility in approximately fifty percent of the blends. Normally, incompatability becomes evident during storage, but sometimes it may be indicated at the time blending occurs, by color changes and residue formation.

It has been demonstrated repeatedly that Du Pont Fuel Oil Additive No. 2 will overcome incompatibility. It has shown effective performance in a wide variety of fuel blends regardless of crude source, processing, or proportions of the components blended. Typical data showing the effect of FOA-2 in preventing or overcoming incompatibility are shown in Figure 3. Because of this versatility, Du Pont FOA-2 is considered and used by many refiners to insure that their fuel will be protected against sludging which may occur in handling and use beyond their control. This is of particular importance to railroads because they often purchase their fuel from many different suppliers.

FIGURE 3

FOA-2 OVERCOMES INCOMPATIBILITY OF CAT-CRACKED, STRAIGHT RUN BLENDS



- Color Stability

For many years the color of a fuel oil has been considered indicative of its quality because it was a property that was readily apparent. A darkening color was believed to be an indication of residue deposition to come later. Indeed, there was a basis in fact on this point with thermal cracked fuels since these fuels would darken rapidly and prove unstable in storage.

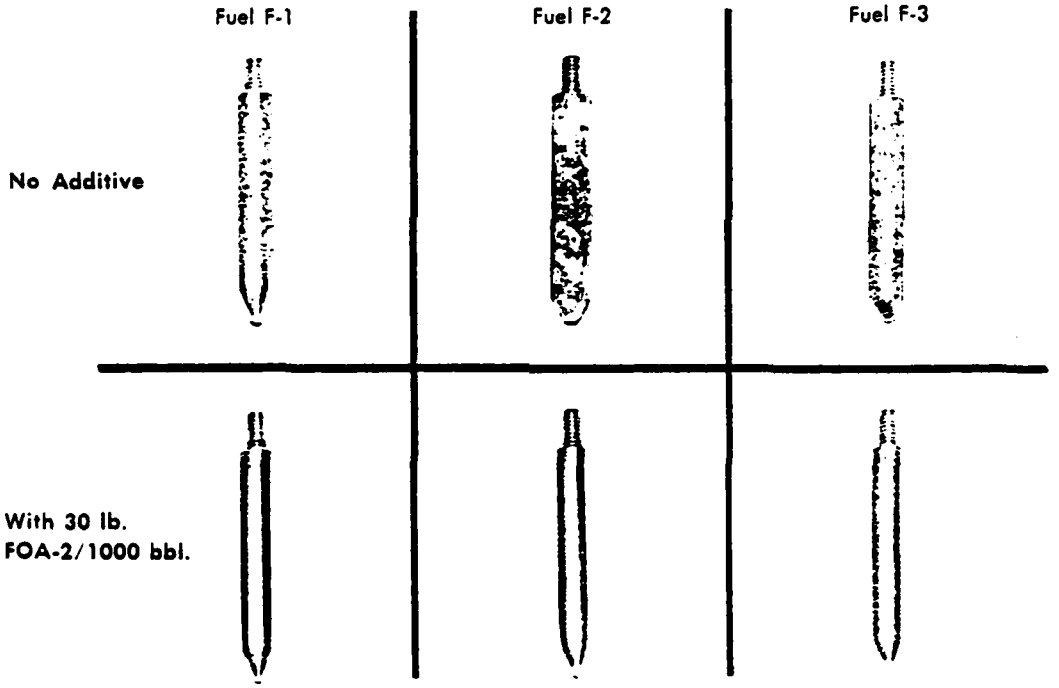
However, the use of dispersant additives in fuel oils to improve their performance has completely changed this concept, since dispersants will suspend and partially solubilize sludges which would otherwise drop out of the fuel and, in doing so, cause the fuel color to be as dark as the uninhibited fuel, or darker.

Du Pont Fuel Oil Additive No. 2 is not usually considered to be a color stablizer under ordinary commercial conditions. In certain high temperature accelerated tests, however, high dosages of the additive will improve the color of the product.

• Corrosion Protection

In addition to its action in improving the stability of fuels, Du Pont Fuel Oil Additive No. 2 provides some corrosion protection. This is illustrated in the ASTM Turbine Oil Rust Test, examples of which are shown in Figure 4.

FIGURE 4
FOA-2 PROVIDES RUST PROTECTION IN ASTM TURBINE OIL RUST TEST

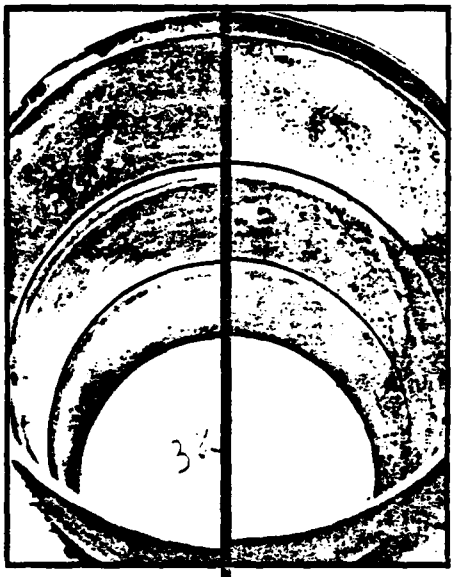


Du Pont FOA-2 prevented rust formation in the interiors of drums used in a drum storage test program. Figure 5 is a composite photograph of the interiors of two drums, one of which contained oil with FOA-2 and the other unstablized oil. Both drums were opened after having been in storage for 7 1/2 months. Rusting on the drum interior developed mainly above the surface of the oil where daily variations in temperature caused water vapor condensation. This rusting was reduced by the use of the additive.

When greater rust protection is required than FOA-2 provides, a commercial corrosion inhibitor may be used. The commercial inhibitors are compatible with the Du Pont additive, and when one is used in combination with FOA-2, less of the corrosion inhibitor is usually needed.

FIGURE 5
FOA-2 REDUCES RUSTING
7½ Months Storage

Fuel F-18



With 30 lb. FOA-2, 1000 bbl. | No Additive

- Use in Combination with Secondary Additives

Du Pont Fuel Oil Additive No. 2 may be used with other dispersants and antioxidants, corrosion inhibitors, dyes and metal deactivators without fear of incompatibility. Du Pont Metal Deactivator (DMD) is used frequently with Du Pont FOA-2 for the prevention of gel formation. The gels consist mainly of fuel oil that has been thickened by copper mercaptides and they may cause as much trouble in fuel systems as insoluble residues. These gels are not, however, related to the insoluble residues. Du Pont Metal Deactivator prevents the formation of copper mercaptides and consequently the gels do not form. Detailed information is available in a separate brochure, "Du Pont Metal Deactivator."

COMMERCIAL APPLICATIONS

- Home Heating Fuels

Insoluble residues which form in home and industrial heating fuel oils, as they age, can combine with fuel and water to form sludge. These sludges can be troublesome in fuel tanks and throughout fuel systems as they cause filter-plugging, restriction of fuel flow and contribute to nozzle-fouling. Burner systems having low feed rates and small nozzle slots are particularly susceptible to operational difficulties due to sludge.

Du Pont Fuel Oil Additive No. 2 has proved to be highly effective in overcoming field sludge problems. Since its first commercial use in 1951, FOA-2 has been used in over one and a half billion barrels of No. 2 distillate fuel for home burner, diesel or other use. Figure 6 shows two cotton rope type filters from a large scale field test with Du Pont FOA-2. Dramatic improvement in filter performance, when the additive has been used, has been repeatedly demonstrated.

FIGURE 6
FOA-2 RETARDS FILTER CLOGGING

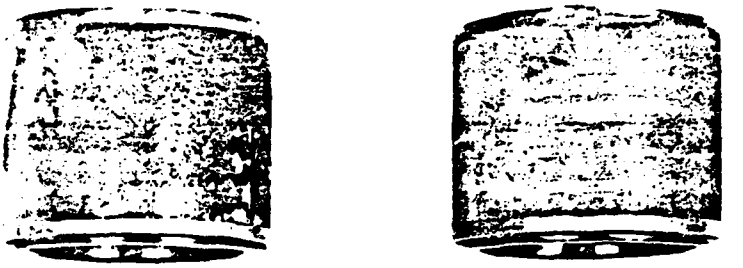
Untreated Oil
1,800 Gal. Throughput

With 30 lb. FOA-2, 1000 bbl.
1,800 Gal. Throughput

The effectiveness of Du Pont Fuel Oil Additive No. 2 has been shown in bench tests using a commercial pump and strainer of the type used in many home burners. In these tests, additive was injected into the fuel either before or after many months' aging in a drum, and the fuel then circulated through a Sundstrand screen. The anti-screen-clogging effect of the additive is shown under both conditions in Figures 7 and 8.

FIGURE 7

FOA-2 REDUCES SCREEN CLOGGING WHEN ADDED PRIOR TO AGING



Control — With 30 lb. FOA-2 1000 bbl.

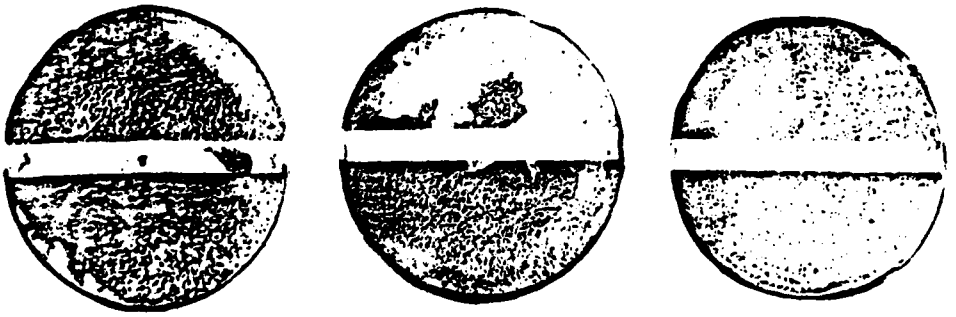
Fuel F-18 Aged 6 Months at 110°F.

Control — With 60 lb. FOA-2 1000 bbl.

Fuel F-19 Aged 9 Months At Room Temperature

FIGURE 8

FOA-2 REDUCES SCREEN CLOGGING WHEN ADDED TO AGED FUEL

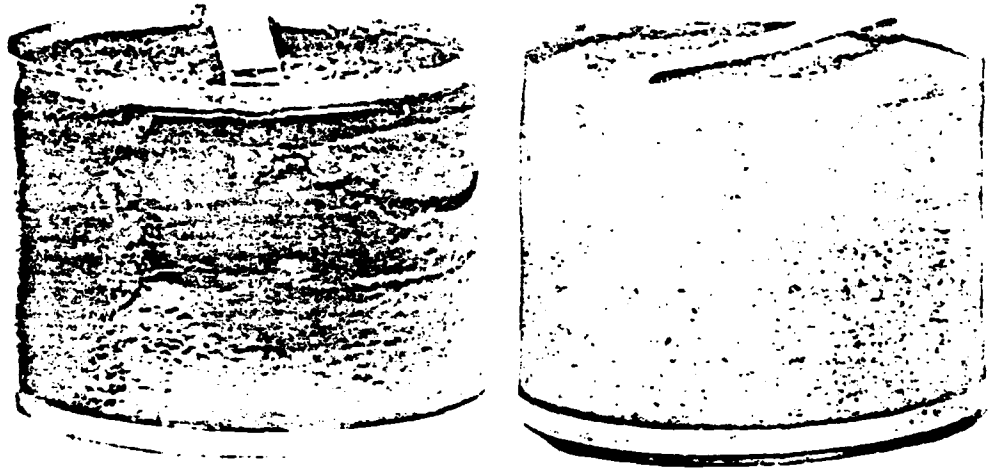


No Additive — With 7.5 lb. FOA-2 1000 bbl. — With 30 lb. FOA-2 1000 bbl.

In one fuel containing FOA-2, the amount of insoluble residue formed, after long storage, equalled that in the uninhibited fuel. However, in this case, the additive kept the sludge particles small and well dispersed, so that filterability was greatly improved by the FOA-2. See evidence of this in Figure 9.

FIGURE 9

FOA-2 IMPROVES FILTERABILITY OF FUEL AFTER STORAGE BY DISPERSING INSOLUBLE RESIDUES



No Additive
Insoluble Residue 9.3 mg./100 ml.

With 30 lb. FOA-2 1000 bbl.
Insoluble Residue 9.5 mg./100 ml.

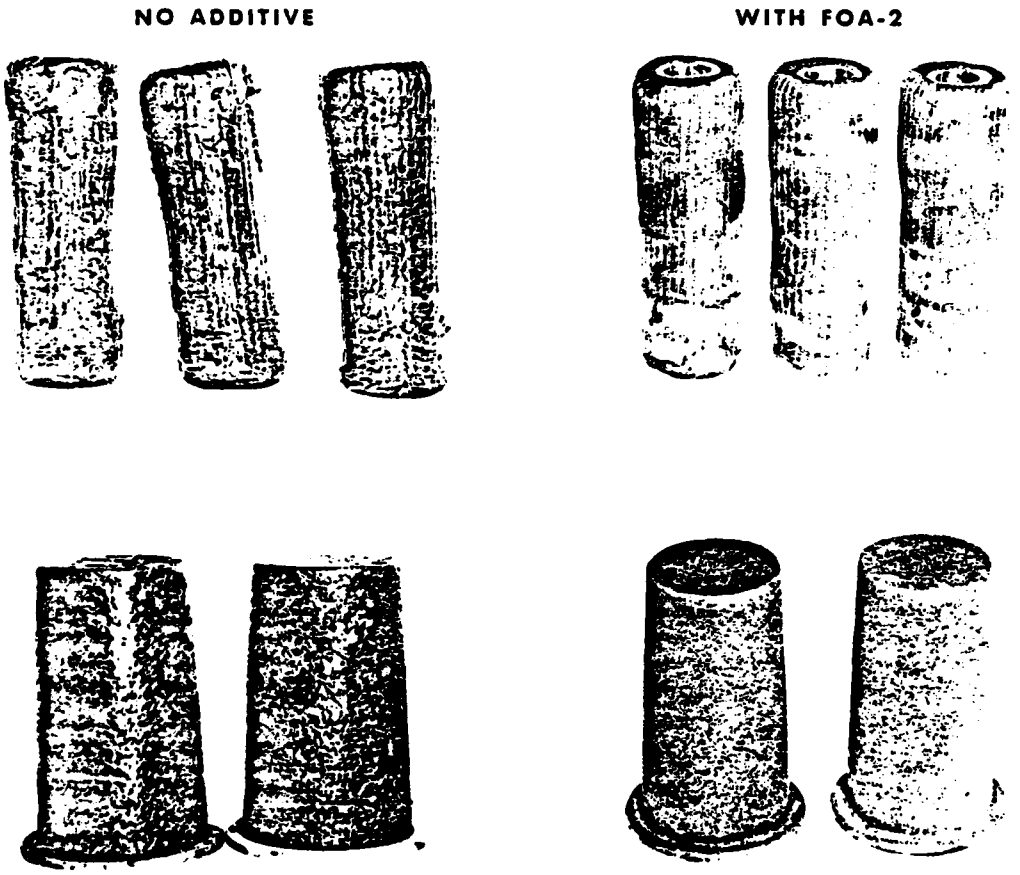
- Diesel Fuels

Instability has been a universal problem with the diesel fuels containing cracked components and has manifested itself in the plugging of filters. This occurs during locomotive fueling and also on diesel engines. Instability also can lead to injector-sticking. Incompatibility of fuels has been one of the major stability problems of the railroads due to the fact that a wide variety of fuel blends are used and that some locomotives are equipped with dual fuel systems which supply distillate fuels for light-load operation and residual fuels for high power outputs.

Diesel fuel troubles due to incompatibility and instability can be avoided by the use of FOA-2. Millions of barrels of railroad "economy" diesel fuels have been treated with FOA-2, and frequently with DMD, the latter to overcome the detrimental effects of copper fuel lines and bronze filters. The favorable reception of FOA-2 in diesel fuels was due to its remarkable effectiveness, as well as to its ashless quality. Being an ashless, nonmetallic dispersant, Du Pont Fuel Oil Additive No. 2 does not contribute to deposits. An example of the effectiveness of FOA-2 in a railroad diesel fuel is shown in Figure 10.

FIGURE 10

FOA-2 RETARDS FILTER PLUGGING IN DIESEL LOCOMOTIVES



Du Pont Fuel Oil Additive No. 2 is also notably successful in preventing injector-sticking due to varnish and sludge formation at the high temperatures of the injector. A portion of the excellent performance is due to the prevention of filter plugging and subsequent "fuel starvation" at the injectors, which increase the temperature due to the restricted flow of fuel for cooling. In addition, FOA-2 minimizes the formation of varnish at high temperatures. This is shown by the data below, obtained on a bench injector-sticking test which utilizes a unit injector heated to 400 F as a small fuel pump.

FOA-2 INHIBITS DIESEL INJECTOR-STICKING

Fuels*	Additive Concentration lb/1000 bbl	Hours to Sticking in Bench Injector Test
100% Cat. Cracked	None	72
	30 lb FOA-2	> 180
Economy Diesel A	None	32
	30 lb FOA-2	> 72**
Economy Diesel B	None	24
	30 lb FOA-2	> 107**

* These inhibited fuels also contained 2 lb DMD/1000 bbl
** Fuel supply exhausted

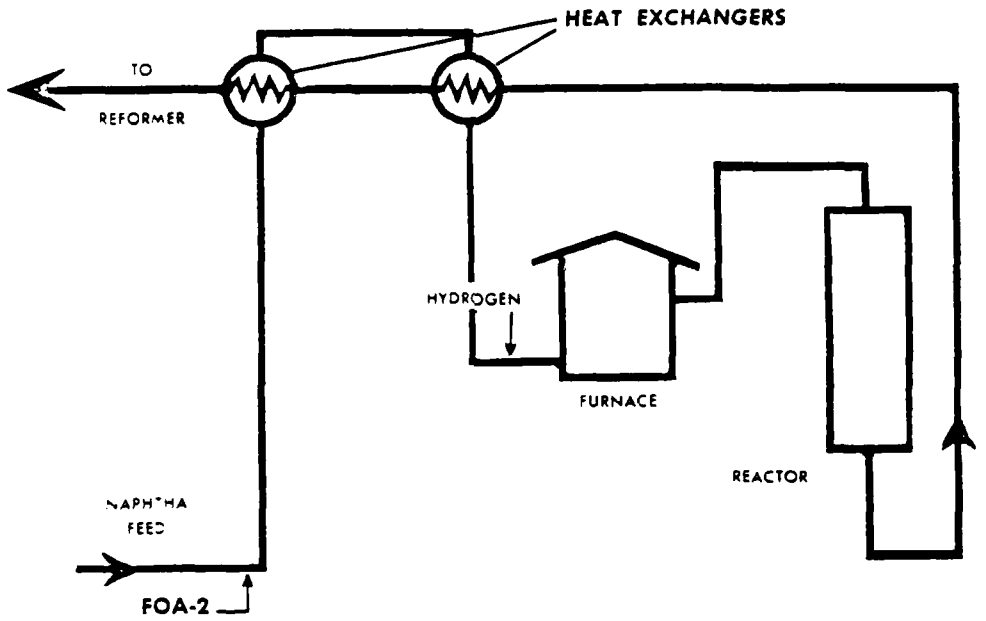
- Heat Exchanger Fouling

Fouling has been fairly common in the heat exchangers of catalytic treaters used prior to catalytic reforming operations. The feed pumped through these exchangers is subjected to temperatures in the range of 400-600 F and pressures of 100-300 psi and under these conditions, the unstable compounds in the feed are deposited on the tubes of the exchanger. Du Pont FOA-2 is effective in reducing these deposits. The effect depends on the feed stocks and the conditions of use.

A flow diagram of a typical refinery heat exchanger setup in which FOA-2 helped overcome fouling is shown in Figure 11.

FIGURE 11

FOA-2 MINIMIZES HEAT EXCHANGER FOULING



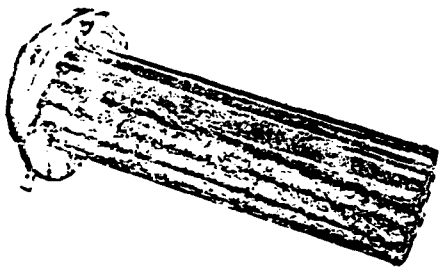
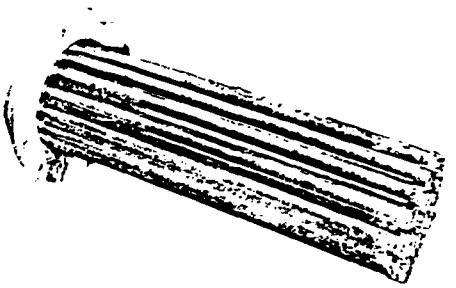
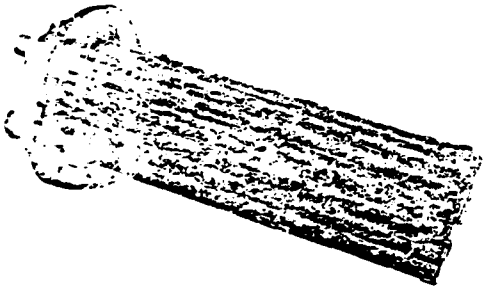
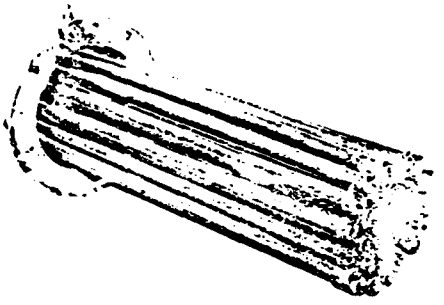
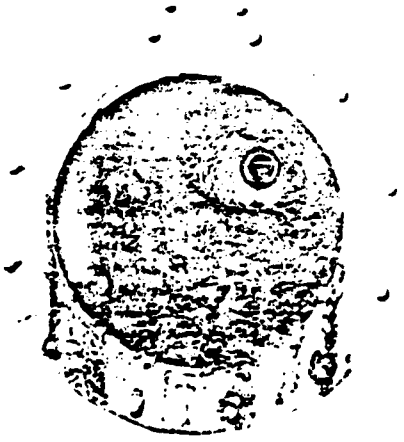
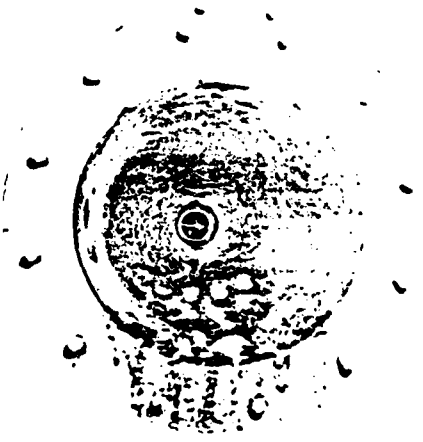
- Residual Fuels

The beneficial effects of Du Pont Fuel Oil Additive No. 2 are not limited to distillate fuels. Marked improvements in the performance of heavy fuels can be obtained through the use of this additive.

Heavy fuels such as No. 5, No. 6 and Bunker C, represent a large portion of the fuel oil market. These fuels retain much of the original impurities in the crude which have not been removed during the refining process. Because of this, there are a number of problems such as tank sludging, strainer and heat exchanger clogging, and burner fouling which are troublesome to the consumer of these fuels. Du Pont Fuel Oil Additive No. 2 is effective in overcoming these sludge problems in heavy fuels. In many instances, expensive shutdowns and maintenance operations can be minimized at low cost through the use of this additive.

FIGURE 12

FOA-2 CLEANS PREHEATERS IN HEAVY FUEL SYSTEMS

	START OF TEST	AFTER 6 MONTHS WITH 20 LB. FOA-2 1000 BBL.
Top		
Bottom		
Shell		

Case histories of the successful use of Du Pont FOA-2 in residual fuels are available in a separate brochure. Typical of these is the improvement effected in the cleanliness of the heavy fuel oil preheater shown in Figure 12.

It is of particular significance that the sludge removal from tanks, filters, and heat exchangers, brought about by FOA-2 is not accompanied by increased or aggravated sludging problems at other points in the fuel system.

PRECAUTIONS IN HANDLING

Tests on animals show that Du Pont Fuel Oil Additive No. 2 has an acute oral toxicity approximately equal to kerosine. The product is only slightly more irritating to the skin than kerosine, which is used as a diluent. No special precautions are required in handling.

SHIPPING INFORMATION

The standard package for FOA-2 is a non-returnable 55-gallon steel drum containing 375 lb net and having a tare weight of 50 lb. Drum shipments are made from Deepwater, New Jersey, and the following warehouses:

Billings, Montana	Kansas City, Missouri
Chicago, Illinois	Los Angeles, California
Mt. Vernon, Washington	Houston, Texas

Amounts smaller than the standard package are available upon request. Bulk shipments are available by tank car or tank truck from Deepwater, New Jersey.

DUPONT

Petroleum Chemicals

FOA-11

FUEL OIL ADDITIVE No. 11

Fuel Oil Additive No. 11 (FOA-11) combines the outstanding antioxidant and color-stabilizing properties of FOA-3, the excellent detergency and dispersancy of FOA-2, and the metal deactivating properties of Du Pont Metal Deactivator in one ashless, easily-handled product.

USE CONCENTRATIONS

Recommended use concentrations for FOA-11 will vary with the fuel and the performance requirements. It is expected that the concentration will be from 5 to 30 lb/1000 bbl (18 to 105 ppm) of fuel oil or diesel fuel.

PHYSICAL PROPERTIES

FOA-11 is an amber colored liquid having an amine odor and is characterized by the following typical properties:

Specific Gravity, 60/60 F (16 C)	0.88
Pounds per gallon, 60 F (16 C)	7.3
Ash, wt. %	0.00
Color, ASTM	L2.5
Flash Point	
Tag Open Cup	120 F (49 C)
Cleveland Open Cup	140 F (60 C)
Pensky-Martens Closed Cup	110 F (43 C)
Fire Point	
Cleveland Open Cup	140 F (60 C)
Pour Point	−55 F (−48 C)
Base Number (TBN-E), mg KOH/g	130
Acid Number (TAN-E), mg KOH/g	0.07
Solubility in Kerosine	Completely soluble
Solubility in No. 2 Fuel Oils	Completely soluble
Solubility in Jet Fuels	Completely soluble

Viscosity:

Temperature	SUS	cSt
0 F (−18 C)	3675	798
32 F (0 C)	1511	328
80 F (27 C)	563	122
100 F (38 C)	416	89.7
210 F (99 C)	133	27.9

PERFORMANCE IN LABORATORY STABILITY TESTS

FOA-11 retards the formation of color and other degradation products in fuel oils. In laboratory accelerated storage stability tests, FOA-11 treated fuels show significantly less insoluble residue formation and better color stability than untreated fuels. The data accumulated in such tests and brief descriptions of the test procedures are presented in the following sections:

ASTM Method D2774 Accelerated Stability Test for Distillate Fuel Oil (Appendix 16, 1961 ASTM Standard on Petroleum Products)

This procedure involves ageing fuel at 203 F (95 C) for 16 hours while oxygen is bubbled through the sample. Reductions in insolubles and color stabilization were obtained by the use of FOA-11 in the test as shown below:

FOA-11 IMPROVES THE STABILITY OF FUEL OILS IN THE PROPOSED ASTM TEST

FOA-11 Concentration, lb/1000 bbl	Total Insolubles, mg/100 ml					Filtrate Color – ASTM (Initial Color In Parenthesis)				
	Fuel					Fuel				
	H	I	J	M	N	H	I	J	M	N
						(L1.0)	(L1.5)	(L1.5)	(1.0)	(1.0)
0	3.7	0.8	1.5	7.9	1.8	3.0	L2.5	L3.0	6.0	3.0
5	–	–	–	2.8	0.7	–	–	–	4.0	2.0
7.5	1.0	0.5	0.5	–	–	L2.5	L1.5	L2.5	–	–
15	0.6	–	–	0.4	0.2	2.0	–	–	2.5	L2.0
25	–	–	–	0.1	0.3	–	–	–	L2.5	L2.0

300 F Accelerated Fuel Oil Stability Test Du Pont Petroleum Laboratory Method F21-61

In this procedure, samples are aged for 90 minutes at 300 F, (149 C), allowed to cool, and filtered through paper. Performance of the fuels is expressed in terms of a visual rating scale of 1 to 20 based on the amount of material on the filters. The lower the rating the more stable the fuel. Many fuels exhibit excellent response to FOA-11 in this test as shown in the following tables.

FOA-11 IMPROVES HIGH TEMPERATURE STABILITY IN THE 300 F TEST

FOA-11 Concentration, lb/1000 bbl	Filter Rating (1 = clean)									
	Fuel									
	A	B	C	E	G	H	J	K	L	M
0	13	17	3	13	7	16	13	15	14	20
5	–	–	–	–	–	–	–	5	–	–
7.5	–	3	2	–	–	–	7	–	–	–
10	–	–	–	–	1	–	–	–	6	6
15	2	3	2	5	–	7	–	2	–	3

	Filtrate Color – ASTM									
(Initial)	(0.5)	(L1.0)	(1.5)	(L1.0)	(L1.0)	(L1.0)	(L1.5)	(1.0)	(1.0)	(1.0)
0	L3.5	5.0	2.5	4.0	L5.5	L6.0	5.5	5.5	5.0	D8.0
5	–	–	–	–	–	–	–	L3.5	–	–
7.5	–	3.0	2.0	–	–	–	3.5	–	–	–
10	–	–	–	–	L1.5	–	–	–	L4.0	5.0
15	L2.0	L3.0	2.0	L2.5	–	3.5	–	L2.5	–	3.5

FOA-11 MAINTAINS HIGH TEMPERATURE STABILITY IN THE 300 F TEST EVEN AFTER 110 F STORAGE

FOA-11 Concentration, lb/1000 bbl	Weeks @ 110 F (43 C)	Filter Rating Fuel				Filtrate Color – ASTM Fuel			
		A	B	C	E	A	B	C	E
0	4	15	18	4	17	4.0	D8.0	L3.5	6.0
7.5	4	–	4	2	–	–	L4.5	L3.0	–
15	4	3	4	2	9	L2.5	L4.0	L3.0	L3.5
0	8	17	20	12	17	L4.5	D8.0	L4.5	D8.0
7.5	8	–	7	3	–	–	5.0	L3.5	–
15	8	3	6	3	10	L3.0	L4.5	L3.5	L5.0
0	12	18	20	14	17	L5.0	D8.0	L6.0	D8.0
7.5	12	–	13	5	–	–	L6.5	L4.0	–
15	12	3	9	4	12	L3.0	L5.5	L4.0	6.0

110 F Fuel Oil Storage Test
Du Pont Petroleum Laboratory Method F8-64

In this test, fuel is stored at 110 F (43 C) in vented bottles and periodic determinations are made of changes in significant properties. One week in 110 F (43 C) storage is considered approximately equivalent to one month in normal field storage.

As shown by the data in the following tables, FOA-11 provides good control of insoluble residue, retards color degradation and maintains good filterability in this test.

EFFECT OF FOA-11 ON STORAGE STABILITY IN 110 F STORAGE TEST

FOA-11 Concentration, lb/1000 bbl	Weeks @ 110 F (43 C)	Insoluble Residue, mg/100 ml								
		Fuel								
		A	B	C	D	E	G	H	K	O
0	0	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.1	0.2
0	4	0.3	1.2	0.4	0.8	1.3	0.6	0.5	1.0	0.9
0	8	0.6	9.3	0.4	2.8	6.1	1.2	1.4	2.1	1.7
0	12	0.9	19.1	1.2	3.6	9.7	1.9	2.8	5.9	2.1
5	4	–	–	–	0.8	–	–	–	0.4	–
5	8	–	–	–	1.8	–	–	–	0.8	–
5	12	–	–	–	2.6	–	–	–	1.2	–
10	4	–	0.7	0.4	–	–	0.5	0.7	–	–
10	8	–	0.5	0.3	–	–	0.6	1.3	–	–
10	12	–	0.7	0.5	–	–	1.1	1.5	–	–
15	4	0.2	0.5	0.3	–	0.9	–	0.4	–	0.6
15	8	0.2	0.6	0.2	–	1.3	–	0.6	–	0.5
15	12	0.3	0.6	0.4	–	1.8	–	0.5	–	1.3

FOA-11 Concentration lb/1000 bbl	Weeks @ 110 F (43 C)	Filtrate Color – ASTM								
		Fuel								
		A	B	C	D	E	G	H	K	O
0	0	0.5	L1.0	1.5	L1.0	L1.0	L1.0	L1.0	1.0	1.0
0	4	L1.5	L3.0	L2.0	L1.5	2.0	L2.0	L2.0	L2.5	L2.5
0	8	L2.0	L5.0	L3.0	L3.0	L3.5	L3.0	2.5	3.0	2.5
0	12	L2.5	L5.5	L3.5	3.0	L4.0	L3.5	L3.5	L4.0	L3.5
5	4	–	–	–	L1.5	–	–	–	2.0	–
5	8	–	–	–	L3.0	–	–	–	L3.0	–
5	12	–	–	–	L3.5	–	–	–	L3.5	–
10	4	–	2.5	L2.0	–	–	L2.0	1.5	–	–
10	8	–	L3.5	2.5	–	–	L3.0	2.5	–	–
10	12	–	L4.0	L3.0	–	–	L3.0	3.0	–	–
15	4	L1.5	L2.5	L2.0	–	1.5	–	1.5	–	L2.5
15	8	L2.0	L3.5	2.5	–	3.0	–	2.5	–	2.5
15	12	L2.5	L3.5	L3.0	–	L3.5	–	L3.0	–	3.0

FOA-11 MAINTAINS EXCELLENT FILTERABILITY OF FUEL OILS AFTER AGING

FOA-11 Concentration lb/1000 bbl	Weeks @ 110 F (43 C)	Minutes to Filter Successive 25 ml Fuel Increments Through Whatman No. 4 Paper					
		1	2	3	4	5	6
Fuel A							
None	0	1.3	1.3	1.4	1.5	1.6	1.7
None	12	2.0	3.0	3.5	4.3	5.0	5.9
15	12	1.5	1.6	1.6	1.6	1.6	1.8
Fuel B							
None	0	1.5	1.6	1.7	1.7	1.7	1.8
None	12	8.1	13.6	17.8	20+	–	–
7.7	12	1.6	1.9	1.9	2.0	2.1	2.2
Fuel C							
None	0	1.6	1.7	1.7	1.8	1.8	1.8
None	12	1.9	2.3	2.3	2.5	2.7	3.1
7.7	12	1.6	1.9	2.0	2.1	2.1	2.3
17.7	12	1.5	1.7	1.7	1.8	1.9	2.0
Fuel D							
None	0	1.4	1.4	1.5	1.6	1.6	1.7
None	12	4.2	17.4	20+	–	–	–
5	12	2.0	2.4	2.6	3.0	3.0	3.3
Fuel E							
None	0	1.5	1.5	1.5	1.5	1.5	1.5
None	12	5.7	20+	–	–	–	–
13.2	12	1.8	2.2	2.5	2.9	3.3	3.7
Fuel G							
None	0	1.4	1.6	1.6	1.6	1.7	1.7
None	12	2.1	2.7	3.2	3.8	4.5	5.8
11.5	12	1.6	1.9	2.0	2.0	2.0	2.2
Fuel H							
None	0	2.1	2.3	2.3	2.5	2.5	2.6
None	12	3.0	7.3	15.3	20+	–	–
7.3	12	1.9	2.5	3.0	3.7	4.1	5.2
14.6	12	2.6	3.4	4.0	4.7	5.3	6.2
Fuel K							
None	0	1.6	1.6	1.6	1.6	1.6	1.6
None	12	9.2	13.6	17.4	18.8	19.0	19.3
5	12	2.3	2.3	2.4	2.5	2.5	2.6
15	12	2.0	2.1	2.1	2.2	2.2	2.2
Fuel O							
None	0	1.8	1.8	1.9	2.0	2.0	2.0
None	12	2.3	3.2	4.5	6.7	10.1	17.4
15	12	1.3	1.4	1.6	1.7	1.8	1.8
30	12	1.5	1.6	1.6	1.8	1.8	1.8

Great Lakes Pipeline Accelerated Stability Test for No. 2 Fuel Oils

In this test, samples of fuel oil are aged 16 hours at 212 F (100 C) under 100 psig oxygen in a bomb, then cooled, filtered and the soluble, insoluble and total gum determined. The color of the filtrate is also measured.

FOA-11 is effective in reducing gum formation and retarding color degradation in this test.

FOA-11 RETARDS GUM FORMATION IN THE GREAT LAKES PIPELINE TEST

FOA-11 Concentration, lb/1000 bbl	Gum, mg/100 ml			
	Soluble	Insoluble	Total	ASTM Color
Fuel A				
None	18.6	6.8	25.4	L5.0
15	7.2	2.6	9.8	3.0
Fuel B				
None	78.1	37.6	115.7	7.5
7.7	40.5	10.3	50.8	6.0
17.7	46.7	4.8	51.5	7.0
Fuel C				
None	59.0	18.0	77.0	L6.0
7.7	26.4	5.2	31.6	L5.0
17.7	24.0	4.2	28.2	L5.0
Fuel D				
None	26.4	14.4	40.8	5.5
5	26.8	10.6	37.4	L5.0
Fuel E				
None	52.4	35.4	87.8	L6.5
13.2	32.0	6.0	38.0	L6.5
Fuel G				
None	22.1	4.9	27.0	L5.5
11.5	7.8	2.4	10.2	L3.0

TEST FUELS

A brief description of the fuels used in the tests described in this bulletin is given below:

A – Diesel, 65% LCO and 35% SR, Mid-Continent

B – Blend of 90% LCO, 10% kerosine, Mid-Continent

C – Blend of 90% LCO, 10% Hydro Bottoms, Mid-Continent

D – Blend of 65% LCO, 35% No. 1 burner fuel, Mid-Continent

E – Blend of 65% LCO, 35% No. 1 burner fuel, Mid-Continent

F – No. 2 fuel oil blend

G – No. 2 fuel oil; 80% CC and 20% SR

H – No. 2 fuel oil; 52% sweet LCO, 25% No. 1 burner oil, 8% Wyoming distillate, 5% Michigan distillate, 5% Unifiner distillate, and 5% Platformer Prefract Bottoms.

I – No. 2 fuel oil blend

J – 50/50 laboratory blend of Fuels H and I

K – No. 2 fuel oil; 80% CC and 20% SR

L – No. 2 fuel oil blend

M – No. 2 fuel oil blend, Gulf Coast

N – 43% Range Oil, 57% LCO

O – No. 2 fuel oil blend

TOXICITY AND PRECAUTIONS IN HANDLING

Although the toxicological properties of FOA-11 have not been fully investigated, other compounds of related chemical structure are toxic and, therefore, FOA-11 should be treated as hazardous material. Excessive inhalation of its vapor should be avoided, and the product should be handled only in locations with good ventilation. FOA-11 contains a caustic material which can cause skin irritation and burns. Contact with skin and eyes should be avoided by use of gloves and goggles. In case of contact with eyes, flush thoroughly with water and get medical attention. Spills on the skin must be washed off immediately with soap and water. Contaminated clothing should be laundered before reuse.

PACKAGES AND SHIPPING POINTS

The standard package for FOA-11 is a nonreturnable 55-gallon steel drum containing 375 pounds net and having a tare weight of 50 pounds. Drum shipments are made from the following locations:

Deepwater, New Jersey	Kansas City, Missouri
Billings, Montana	Los Angeles, California
Chicago, Illinois	Houston, Texas

Amounts smaller than the standard package are available upon request.

Bulk shipments are available by tank car or tank truck from Deepwater, New Jersey.

DU PONT

Petroleum Chemicals

AO-22

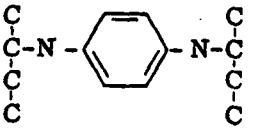
ANTIOXIDANT No. 22

Du Pont Antioxidant No. 22 (Du Pont AO-22) is an additive used to inhibit the oxidation of motor and aviation gasolines and jet fuels. Du Pont AO-22 is also used to catalyze the sweetening of sour blending stocks and gasoline blends. The normal concentration range is 2 to 10 lb/1000 bbl (approximately 8 to 40 ppm) in finished blends. Dosage levels up to 20 lb/1000 bbl (80 ppm) are frequently employed to inhibit severely cracked blending stocks such as pyrolysis and coker gasolines.

Du Pont AO-22 has been approved under the following military and ASTM specifications:

Automotive Gasoline	-	MIL-G-3056
Aviation Gasoline	-	MIL-G-5572 and ASTM D 910
Jet Fuel	-	MIL-T-5624, MIL-T-5161, MIL-P-25576,

COMPOSITION AND TYPICAL PROPERTIES

Active Ingredient, 100 wt.%	Principally N,N'-di-secondary butyl-para-phenylenediamine.
Structural Formula	
Physical Form	Red Liquid
Specific Gravity, 60/60 F (16/16 C)	0.94
Density, lb/gal 60 F (16 C)	7.8
Solidification Temperature	Will solidify at 68 F (20 C) if seeded. Unseeded it can be super-cooled to below -10 F (-23 C)
Flash Point, Pensky-Martens Closed Cup	>200 F (93 C)
Thermal Decomposition	Above 450 F (232 C)
Solubility in gasoline, 80 F (27 C)	All proportions
Solubility in water, 80 F (27 C)	0.06 wt.%

Viscosity:	Temperature	SUS	cSt
	100 F (38 C)	64	11
	77 F (25 C)	107	22
	32 F (0 C)	687	149

MECHANISM OF OXIDATION AND FUNCTION OF ANTIOXIDANT

The primary function of an antioxidant in gasolines is to retard the formation of gum and the precipitation of lead alkyl antiknocks.

Gum is the product of a series of oxidation and polymerization reactions involving principally the olefinic constituents present in cracked gasolines. The oxidation attack occurs first on the least stable components of the gasoline, forming products which are capable of initiating oxidation of more stable compounds.

The initial products formed during oxidation of gasoline are free radicals. These may react with oxygen to form peroxy free radicals which in turn react with the hydrocarbons to form hydroperoxides and hydrocarbon free radicals. Thus, oxidation, once started, can proceed as a chain reaction. The hydroperoxides may decompose directly into more stable compounds or may give rise to free radicals which are capable of propagating the oxidative chain and are active in causing precipitation of lead antiknock compounds.

The oxidation reactions may be represented by the following equations:

1. CHAIN INITIATION

$$R\text{-}H \longrightarrow R\cdot + H\cdot$$

2. CHAIN PROPAGATION

a. $R\cdot + O_2 \longrightarrow R\text{-}O\text{-}O\cdot$

b. $R\text{-}O\text{-}O\cdot + R'\text{-}H \longrightarrow R'\cdot + R\text{-}O\text{-}O\text{-}H$

Antioxidants terminate these chain reactions as shown below by reacting with free radicals and peroxides to form compounds of low energy content which are stable and do not initiate or propagate further chain reactions.

$$ROO\cdot + \text{Antioxidant} \longrightarrow ROOH + \text{Antioxidant free radical}$$

PERFORMANCE OF DU PONT AO-22

The ability of Du Pont AO-22 to protect gasolines from oxidation, as measured by ASTM Oxidation Stability of Gasoline Method D-525 is shown in the Tables below. These data indicate Du Pont AO-22 is highly effective in stabilizing a wide variety of fuels. In Table I the data are shown in terms of induction period obtained with given amounts of additives while Table II shows the amount of additive required for a given induction period. Both tables show comparisons with Du Pont AO-23 and two competitive antioxidants, GAO-2 and GAO-3.

TABLE I

EFFECT OF DIFFERENT ANTIOXIDANTS ON
ASTM INDUCTION PERIOD OF SEVERAL GASOLINES

Additive	Gasoline -	ASTM D525-55 Induction Period-Minutes A	B	C	D	E
No Additive		80	145	210	220	655
2 lb Antioxidant/1000 bbl (8 ppm)						
AO-22		185	365	335	360	805
AO-23		150	305	285	320	750
GAO-2		165	300	310	-	-
GAO-3		125	240	265	300	725
4 lb Antioxidant/1000 bbl (16 ppm)						
AO-22		285	560	450	490	940
AO-23		215	400	355	410	830
GAO-2		265	440	410	-	-
GAO-3		185	330	320	380	795
8 lb Antioxidant/1000 bbl (32 ppm)						
AO-22		505	935	645	720	1080
AO-23		365	620	485	560	990
GAO-2		455	720	610	-	-
GAO-3		295	500	420	505	925

TABLE II

AMOUNT OF DIFFERENT ANTIOXIDANTS REQUIRED
TO OBTAIN SPECIFIED INDUCTION PERIOD OF SEVERAL GASOLINES

Additive	Gasoline -	Antioxidant Dosage - lb/1000 bbl. A	B	C	D	E
Additive for 300 Minutes Induction Period						
AO-22		4.3	1.4	1.5	1.2	*
AO-23		6.3	2.0	2.4	1.6	*
GAO-2		4.8	2.1	1.8	-	*
GAO-3		8.1	3.3	3.3	2.0	*
Additive for 400 Minutes Induction Period						
AO-22		6.1	2.4	3.1	2.7	*
AO-23		8.9	3.7	5.4	3.7	*
GAO-2		6.9	3.3	3.7	-	*
GAO-3		>10.0	5.8	7.2	4.7	*

*Base gasoline exceeded required Induction Period without additive.

NOTE: GAO-2 is N, N'-disecondary-butyl-p-phenylenediamine plus a sweetening catalyst.
GAO-3 is N, N'-dioctyl-p-phenylenediamine
AO-23 is N, N'-diisopropyl-p-phenylenediamine (50% active ingredient)

The effectiveness of Du Pont AO-22 for controlling gum formation in gasolines is illustrated below using both an accelerated test and storage at 110F (43C). Table III provides the 4-hour accelerated test results (Potential Residue Method ASTM D 873), which show that both Du Pont AO-22 and Du Pont AO-23 are highly effective in controlling gum formation. Table IV summarizes storage test data obtained at 110F (43 C), comparing the effectiveness of the antioxidants in controlling gum formation during storage.

TABLE III
PERFORMANCE OF ANTIOXIDANTS IN FOUR-HOUR
ACCELERATED POTENTIAL RESIDUE METHOD (ASTM D 873)

	Total Potential Residue, mg/100 ml	
Antioxidant	Light Cat Cracked Gasoline F	Gasoline Blend G
No Additive	79	77
2 lb/1000 bbl (8 ppm)		
AO-22	-	2
AO-23	-	3
4 lb/1000 bbl (16 ppm)		
AO-22	0	3
AO-23	1	0

TABLE IV
EFFECT OF ANTIOXIDANTS ON GASOLINES STORED
AT 110 F (43 C) (DU PONT PETROLEUM LABORATORY METHOD G34-52)

	Existent Gum, mg/100 ml after Storage at 110 F (43 C), ASTM D381							
Gasoline	D		H		J		K	
Week's Storage*	6	12	6	12	6	12	6	12
No Antioxidant	-	32	54	283	9	-	3	23
2 lb Antioxidant (8 ppm)								
AO-22	-	3	5	11	-	-	2	2
AO-23	-	4	7	10	-	-	1	1
GAO-3	-	3	5	10	-	-	1	1
5 lb Antioxidant (20 ppm)								
AO-22	-	1	1	2	4	-	1	0
AO-23	-	1	2	5	4	-	1	1
GAO-3	-	2	-	5	-	-	1	2

*NOTE: One week's storage at 110 F (43C) is considered approximately equivalent to one month in normal field storage.

High concentrations of antioxidant are required to stabilize some gasoline components. Table V below illustrates the effect of Du Pont AO-22 addition on the stability of coker gasoline.

TABLE V
EFFECT OF DU PONT AO-22
ON THE STABILITY OF COKER GASOLINE

AO-22, lb/1000 bbl	Existent Gum, mg/100 ml	ASTM Induction Period, Minutes	Accelerated Gum 4-hr., mg/100 ml
None	5	15	630
10	2	198	161
20	-	315	31
30	-	430	13

ANTIOXIDANT SWEETENING

An additional consideration in the selection of an antioxidant is its ability to sweeten low mercaptan content cracked gasolines. In many refinery stocks Du Pont AO-22 readily converts mercaptans to less odorous sulfur compounds. This type of treating produces a doctor sweet gasoline and has many advantages, such as:

1. Low initial cost - A substantial saving in basic sweetening equipment is possible through Du Pont AO-22 sweetening.
2. Lower operating costs - While operating costs vary with treating methods the use of Du Pont AO-22 reduces the need for additional chemicals and reduces regeneration expenses.
3. No undesirable chemicals - Since Du Pont AO-22 sweetening does not require the use of sulfur or copper, the chance of contamination from these elements is avoided during the sweetening operation.
4. Stabilization and sweetening combined - These two results are achieved in the single, inexpensive operation of adding Du Pont AO-22 to your stocks.

Sweetening Performance

Du Pont AO-22 is effective as a sweetening catalyst in a variety of refinery gasoline streams. The results of a laboratory study, employing a catalytically cracked gasoline and comparing Du Pont's AO-22 and AO-23 with GAO-3 are summarized graphically in Figure 1, page 6. This gasoline initially contained 0.010 weight percent mercaptan sulfur. The test involved contacting the inhibited gasoline samples with 2 volume percent of 20°Bé used refinery caustic and measuring the rate of mercaptan sulfur reduction.

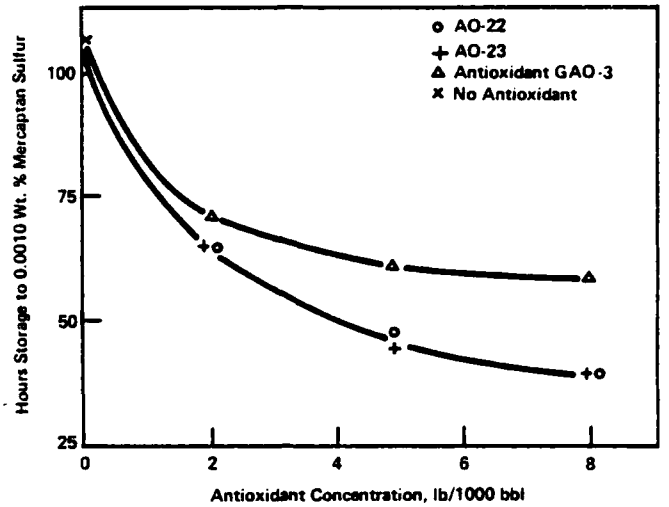


Fig. 1 – Sweetening Rate of a Catalytically Cracked Gasoline.

Sweetening Process Equipment

The equipment required for antioxidant sweetening is relatively simple. In most instances all that is required is a modification of existing equipment. The essential parts are caustic washing facilities, a mixer, and run-down tank, and are illustrated below in Figure 2.

As in any form of treating, the importance of process variables makes it desirable to evaluate each individual case carefully. To provide additional information, a descriptive booklet on Du Pont AO-22 Sweetening has been prepared and may be obtained upon request from your Du Pont representative.

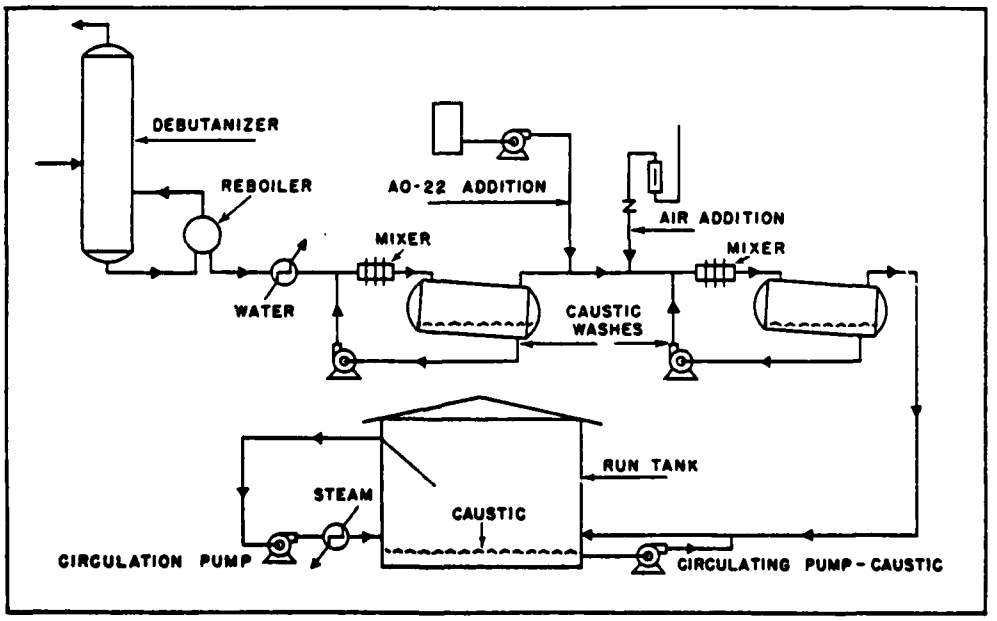


Fig. 2 – Simplified Flow Diagram of Antioxidant Sweetening System.

Field Experience

Even in carefully controlled laboratory tests it is difficult to simulate the conditions which exist in refinery sweetening units. To obtain an accurate evaluation of sweetening performance it is recommended that full scale tests be conducted in the refinery.

WATER AND CAUSTIC EXTRACTIBILITY

The insolubility of Du Pont AO-22 in aqueous media above pH 5.0 is especially useful in certain applications. AO-22 may be added to stocks free from hydrogen sulfide prior to doctor sweetening or caustic washing, thus providing the best possible response through early antioxidant addition. Occasionally gasolines contact acidic water in tanks or pipelines. Under these conditions, Du Pont AO-22 may be partially extracted if sufficient agitation is provided. Extraction data are shown below in Figure 3.

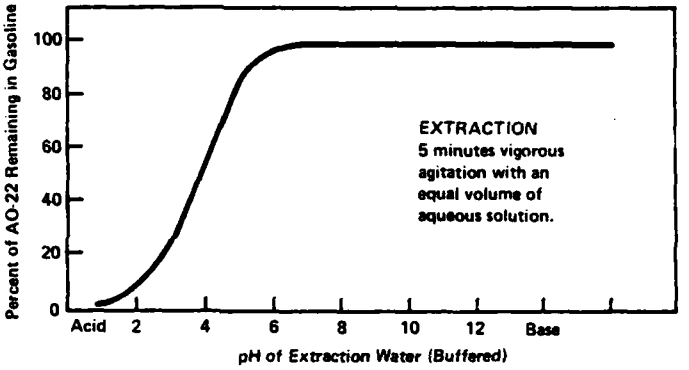


Fig. 3 – Extraction of Du Pont AO-22 From Gasoline.

WATER INTERACTION

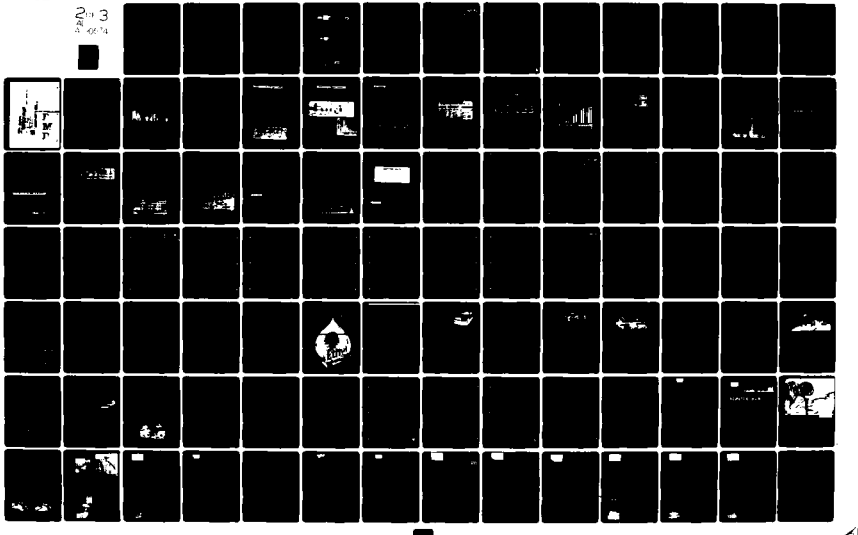
Du Pont AO-22 at its upper use concentrations has no effect on gasoline or jet fuel water interaction.

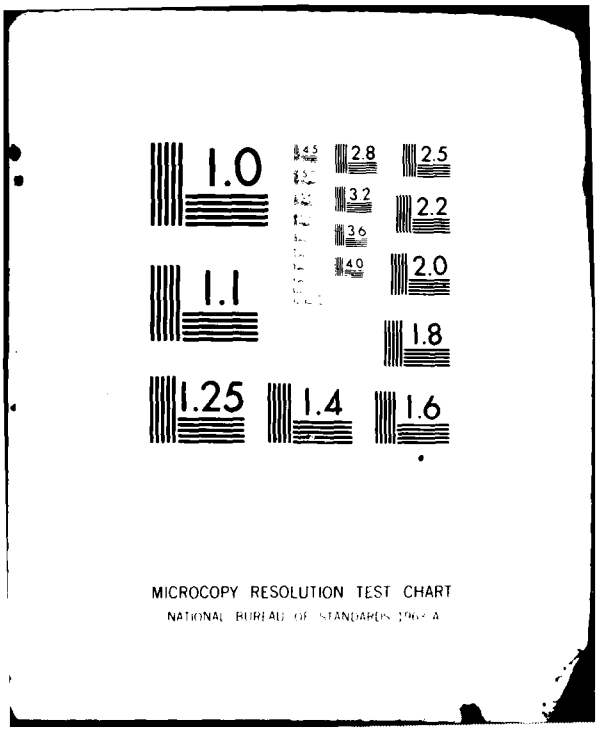
COLOR AND SUNLIGHT STABILITY

The tinctorial effect of Du Pont AO-22 is low, and its addition in concentrations necessary for effective oxidation control does not significantly affect the color of the gasoline. However, when unleaded gasolines containing Du Pont AO-22 are exposed to sunlight for prolonged periods, some darkening of the gasoline may occur.

When leaded gasolines containing Du Pont AO-22 are exposed to sunlight, even for relatively short periods, they develop a red color. This is caused by a photochemical reaction between the antioxidant and the halide scavenging agent in the tetraethyl lead compound.

AD-A110 574 ARMY ENGINEER DIV HUNTSVILLE AL F/G 13/5
ADDITIVES TO PREVENT DELETERIOUS EFFECTS ASSOCIATED WITH LONG-T--ETC(U)
SEP 80 R J LARSON, P G MALONE
UNCLASSIFIED HNDTR-80-50-SP NL




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

COMPATIBILITY

Du Pont AO-22 is compatible in gasoline with other additives including dyes, metal deactivators, rust preventives, and many multifunctional additive packages.

LOW TEMPERATURE PROPERTIES

Du Pont AO-22 contains no solvent and has a true freezing point of approximately 68 F (20 C); however, it is readily supercooled to temperatures considerably below its freezing point without solidifying. When stored below its freezing point, crystallization may be caused by sudden chilling, prolonged storage or seeding with a crystal of antioxidant. Should freezing occur the material may be restored to its original liquid state without loss in effectiveness by heating and occasional rolling of the drums.

Du Pont AO-22 and the equipment for adding it to gasoline should be protected against freezing during use. Where this is not possible, stock solutions are prepared. The curve below shows the degree of solution necessary to insure crystal-free stock solutions of Du Pont AO-22 at various temperatures. The separation temperatures vary in different types of gasolines.

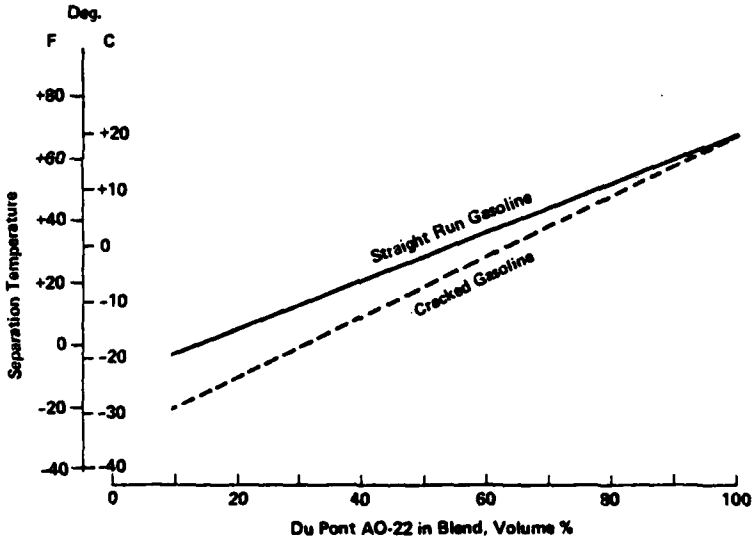


Fig. 4 – Low Temperature Characteristics of Du Pont AO-22/Gasoline Blends.

POINT OF ADDITION

It is desirable to add antioxidants as early as possible. The point of addition will depend somewhat on the refining processes employed and on the antioxidant used.

Antioxidants generally are injected after most treating steps are completed. Except where antioxidant sweetening is employed, addition is usually made to the lines leading from the processing equipment to storage tanks. Where there is an appreciable lapse of time between distillation and subsequent treating steps, it is sometimes desirable to add a small amount of antioxidant to prevent deterioration during this storage period. The insolubility of Du Pont AO-22 in water and caustic makes it particularly suited for this purpose.

METHODS OF ADDITION

The preferred method of antioxidant addition is on a continuous basis in the proper ratio to the flow of product being treated.

Many different types of addition equipment are in use and, while a complete review of the many possible systems is beyond the scope of this bulletin, a few of the more common ones will be described briefly. For specific applications, your Du Pont representative is available for assistance.

"In-Line" Blending

Many modern refineries blend finished gasoline "in-line", with precise control of individual fuel component streams, using digital electronic equipment. As a result, the completed blend is frequently sent directly to a pipeline or ship.

On "in-line" systems, the additive streams are flow-controlled in the same manner. Figure 5 depicts such a system.

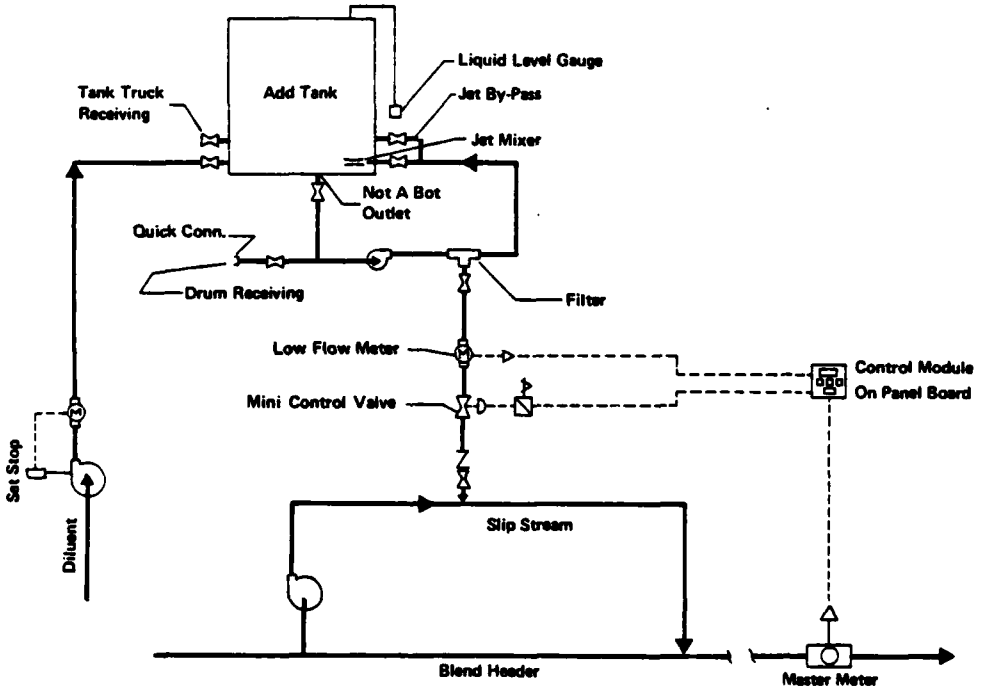


Fig. 5 – Typical Flow-Controlled Antioxidant Addition System for "In-Line" Blender.

Proportioning Pumps

Proportioning pumps are used by many refiners for antioxidant addition. These pumps are all of the positive displacement type but vary in design and, in some cases, in principle of operation.

PRINCIPLES OF OPERATION OF PROPORTIONING PUMPS--In all of the pumps recommended for antioxidant service, a fixed volume of antioxidant is delivered

with each stroke of the piston or revolution of the pump. The quantity of material discharged is adjustable by changing the length of stroke or varying the speed of the pump.

CONSTANT SPEED OPERATION--When the flow of fuel to be inhibited is constant, the pump may be driven by a constant speed motor and the length of the piston stroke adjusted to deliver antioxidant at the desired rate. This is the simplest type of installation and one of these is diagrammed in Figure 6.

FLOW-RESPONSIVE PROPORTIONING--In most refineries the rate of product flow is variable and it is not practical to inject antioxidant at a constant rate. When this situation prevails, automatic control devices are frequently used in conjunction with the proportioning pump to regulate the rate of antioxidant addition. A diagrammatic sketch of such a system is shown in Figure 7. Automatic control systems are of several types and the pump manufacturer can recommend the system best suited for each application.

While several pumps have been specifically designed for automatic operation, all of them may be adapted for use with automatic controls. Since this type of flow is cyclic, the rate is not measured and hence is not remote indicated.

Eductors

Various systems employing an eductor have been used with some success. Illustrated in Figure 8 is a system where Du Pont AO-22 is drawn directly from a drum. The amount of antioxidant used is measured by reading the scale.

PACKAGES AND SHIPPING POINTS

The standard package for Du Pont AO-22 is a non-returnable 55-gallon steel drum containing 425 lbs. net and having a tare weight of 50 lbs. Drum shipments are made from Deepwater, New Jersey and the following warehouses:

Billings, Montana	Los Angeles, California
Chicago, Illinois	Houston, Texas
Kansas City, Missouri	

Amounts smaller than the standard package are available upon request. Bulk shipments are available by tank car or tank truck from Deepwater, New Jersey.

PRECAUTIONS IN HANDLING

Causes burns as defined by D.O.T. Skin Corrosivity Test. Do not get in eyes, on skin, on clothing. Avoid breathing vapor. Use with adequate ventilation. Wash thoroughly after handling.

FIRST AID - In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing clothing and shoes. Call a physician. Wash clothing before reuse.

IN CASE OF FIRE - Use water spray, foam, dry chemical, or CO_2.

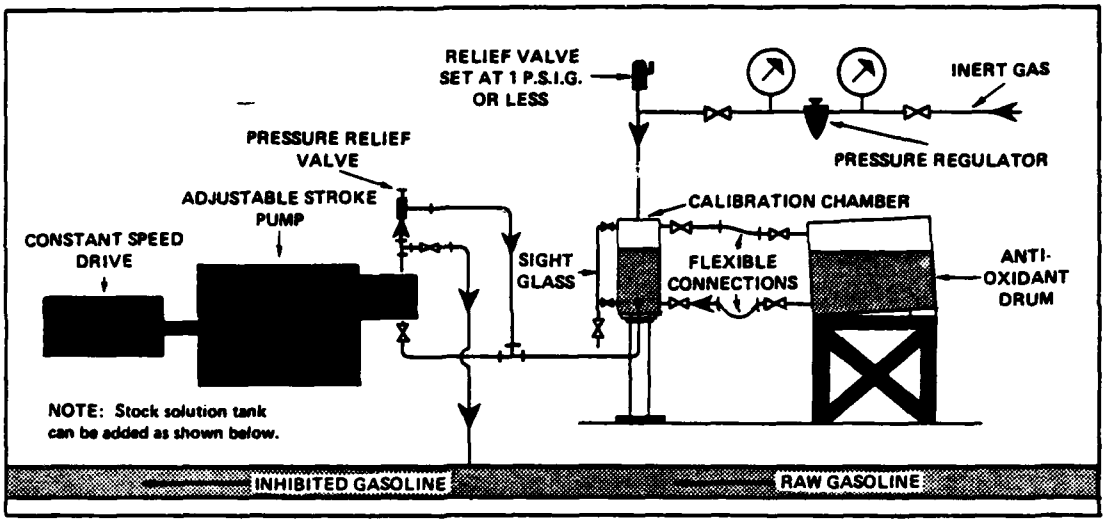


Fig. 6 – Constant Speed Proportioning Pump With Suction Direct From Shipping Container. (Constant Speed Addition).

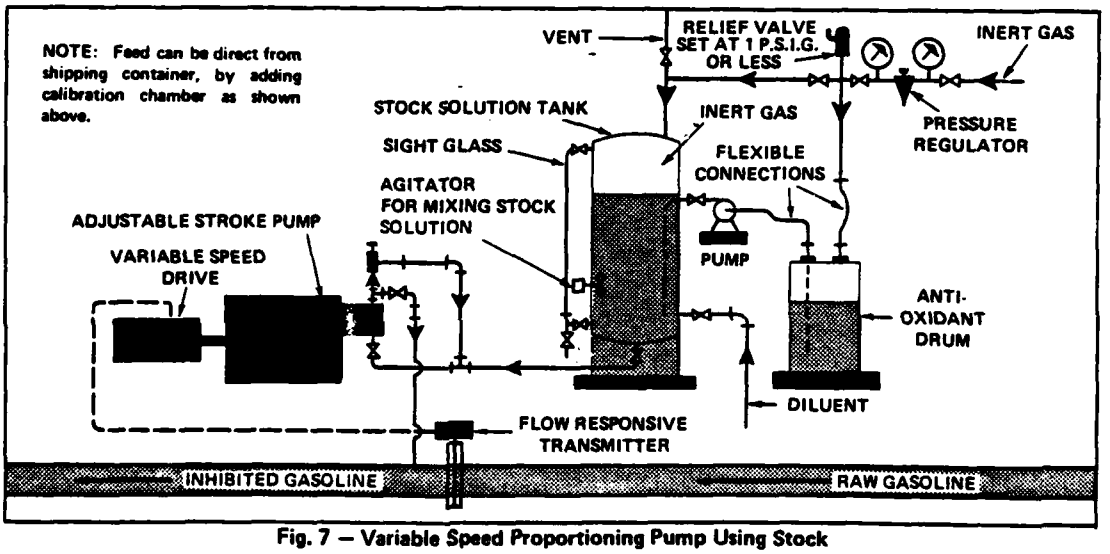


Fig. 7 – Variable Speed Proportioning Pump Using Stock Solution Tank. (Flow-Proportional Addition).

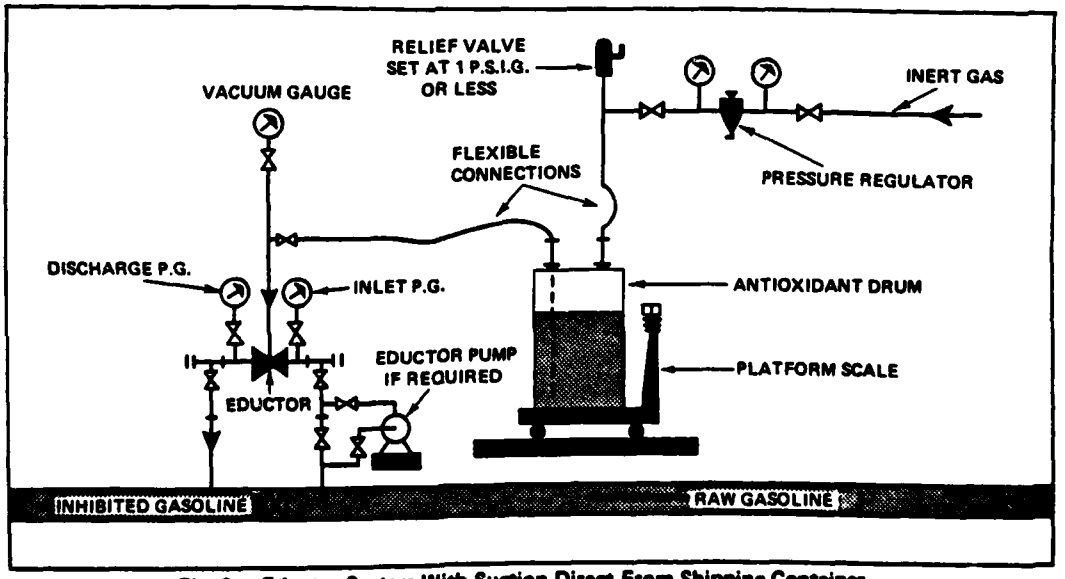


Fig. 8 – Eductor System With Suction Direct From Shipping Container.

Du Pont Petroleum Chemicals
Wilmington, Delaware 19898

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DUPONT

Petroleum Chemicals

AO-35

ANTIOXIDANT NO. 35

Antioxidant No. 35 is a mixture of alkylated phenols. It is effective in inhibiting gum formation and precipitation of lead alkyl compounds in gasolines. AO-35 may also be used to stabilize other light hydrocarbons. For those refiners who prefer an alkylated phenol antioxidant, AO-35 is particularly attractive because, in addition to its low cost relative to other commercially available antioxidants of this type, it offers superior low temperature handling properties. Typical use concentrations are 1 to 10 lb/1000 bbl (4 to 40 ppm).

AO-35 has been approved by the Military for use in:

MIL-G-3056	– Automotive Combat Gasoline
MIL-G-5572	– Aviation Gasolines
MIL-T-5624	– Aviation Turbine Fuels
VV-G-76B	– Gasoline, Automotive
VV-G-001690	– Gasoline, Automotive, Low [illegible] Unleaded

COMPOSITION

Butylated ethylphenols	55% minimum
Butylated methyl and dimethylphenols	45% maximum

TYPICAL PROPERTIES

Physical form	Amber liquid
Sp. Gravity, 60/60°F (16/16°C)	0.96
Pounds per gallon, 60°F (16°C)	8.0
Flash Point, PMCC	202°F (94°C)
Crystallization Temp. (Seeded)	Below −30°F (−34°C)
Pour Point	−20°F (−29°C)

Viscosity

Temperature	SUS	cSt
0°F (−18°C)	144,330	31,350
32°F (0°C)	3,340	724
77°F (25°C)	182	39
100°F (38°C)	84	17

ANTIOXIDANT PERFORMANCE

The effectiveness of AO-35 in protecting motor gasoline against oxidation has been compared with a competitive phenol antioxidant (GAO-4) and Du Pont Antioxidant No. 33 using ASTM D525, Induction Period Method. The data shown in Table 1 indicate that AO-35 effectively controls gasoline stability.

TABLE 1

EFFECT OF ALKYLATED PHENOL ANTIOXIDANTS ON MOTOR GASOLINE STABILITY – ASTM D525, INDUCTION PERIOD METHOD

Gasoline	Pb, g/gal (TEL)	Antioxidant lb/1000 bbl	Induction Period, minutes None	GAO-4	AO-33	AO-35
G-95	0.24	0	269	–	–	–
		5	–	440	395	443
		10	–	545	550	530
G-96	1.65	0	240	–	–	–
		5	–	325	330	317
		10	–	380	390	385
G-97	1.20	0	658	–	–	–
		5	–	712	710	703
		10	–	820	768	825

AO-35 inhibits the formation of gum and lead precipitation in gasoline as measured by ASTM D873, Potential Residue Method. As shown by the data in Table 2, this test method also shows AO-35 to be effective as a gasoline stabilizer.

TABLE 2

EFFECT OF ALKYLATED PHENOL ANTIOXIDANTS ON MOTOR GASOLINE STABILITY – ASTM D873, POTENTIAL RESIDUE METHOD

Gasoline	Pb, g/gal (TEL)	Antioxidant lb/1000 bbl	4-Hour Potential Residue, mg/100 ml None	GAO-4	AO-33	AO-35
G-95	0.24	0	14	–	–	–
		5	–	4.5	4.3	2.7
		10	–	2.5	3.3	1.4
G-96	1.65	0	166	–	–	–
		5	–	109	145	78
		10	–	20	30	27
G-98	0.00	0	23	–	–	–
		5	–	17	30	14
		10	–	10	20	9
G-99	0.00	0	196	–	–	–
		5	–	88	85	75
		10	–	42	31	27
G-44	0.00	0	10	–	–	–
		5	–	13	14	8.0
		10	–	8.5	12	4.5

The data summarized in Table 3 indicate that AO-35 stabilizes aviation gasolines against oxidation as measured by ASTM D873, Oxidation Stability of Aviation Fuels. The performance of a competitive antioxidant GAO-4 in the same gasolines is presented for comparison. While 8.4 lb/1000 bbl is the maximum allowable concentration in aviation gasoline, AO-35 is effective in reducing potential gum and precipitate to values well below specification limits at 3 lb/1000 bbl.

TABLE 3

EFFECT OF ALKYLATED PHENOL ANTIOXIDANTS ON AVIATION GASOLINE STABILITY – ASTM D873, POTENTIAL RESIDUE METHOD

Antioxidant		16-Hour Potential Residue, mg/100 ml Aviation Gasoline			
		100/130 3.0 ml TEL/gal		115/145 4.6 ml TEL/gal	
Type	lb/1000 bbl	Potential Gum	Precipitate	Potential Gum	Precipitate
None	0	57	17	66	84
GAO-4	3	0	0	0.1	0
AO-35	3	0.1	0	0.2	0

Table 4 compares the effectiveness of AO-35 and GAO-4 in a light catalytic gasoline after contact with Unisol solution and aging at 110°F for four weeks. Caustic carryover from the Unisol or other alkaline systems used in refinery processing can result in a decrease in gasoline stability. The presence of AO-35 was responsible for nearly a ten fold increase in induction period under these conditions. Table 4 also summarizes the induction system deposit data on the same samples and shows AO-35 to be superior to GAO-4. The ISD data were developed in a laboratory bench rig where fuel was sprayed onto a steam-heated glass surface. These weights reflect the deposit forming tendency of the gasoline with substantial improvement in fuel quality resulting from the AO-35 addition.

TABLE 4

ANTIOXIDANT AND INDUCTION SYSTEM DEPOSIT (ISD) PERFORMANCE IN LIGHT CATALYTIC GASOLINE CONTACTED WITH UNISOL SOLUTION AND AGED AT 110°F FOR FOUR WEEKS

Antioxidant		ASTM D525	ISD Weight
Type	lb/1000 bbl	Induction Period, min.	mg/liter
None	0	38	1591
GAO-4	10	250	11
AO-35	10	359	7

AO-35 inhibits the formation of gum in gasoline as measured by 110°F (43°C) storage tests. The data are shown in Table 5. The 110°F storage tests correlate well with actual field storage and corroborate the accelerated test data for AO-35.

TABLE 5

EFFECT OF ALKYLATED PHENOL ANTIOXIDANTS ON MOTOR GASOLINE STABILITY IN 110°F STORAGE TESTS

			Existent Gum, mg/100 ml Weeks to Form		
	Antioxidant				
Gasoline	Type	lb/1000 bbl	5 mg	10 mg	20 mg
G-44	None	0	3	7	9
	GAO-4	2	5	9	15
	AO-35	2	4	9	14

METHODS OF HANDLING AND ADDITION

AO-35 is soluble in gasolines in all proportions and may be added directly to gasoline or as a gasoline stock solution.

In cold climates the viscosity of AO-35 can be reduced by addition of xylene or other refinery solvents. Viscosity data for AO-35 and AO-35/xylene blends are shown in Table 6 and in Figure 1 on page 5.

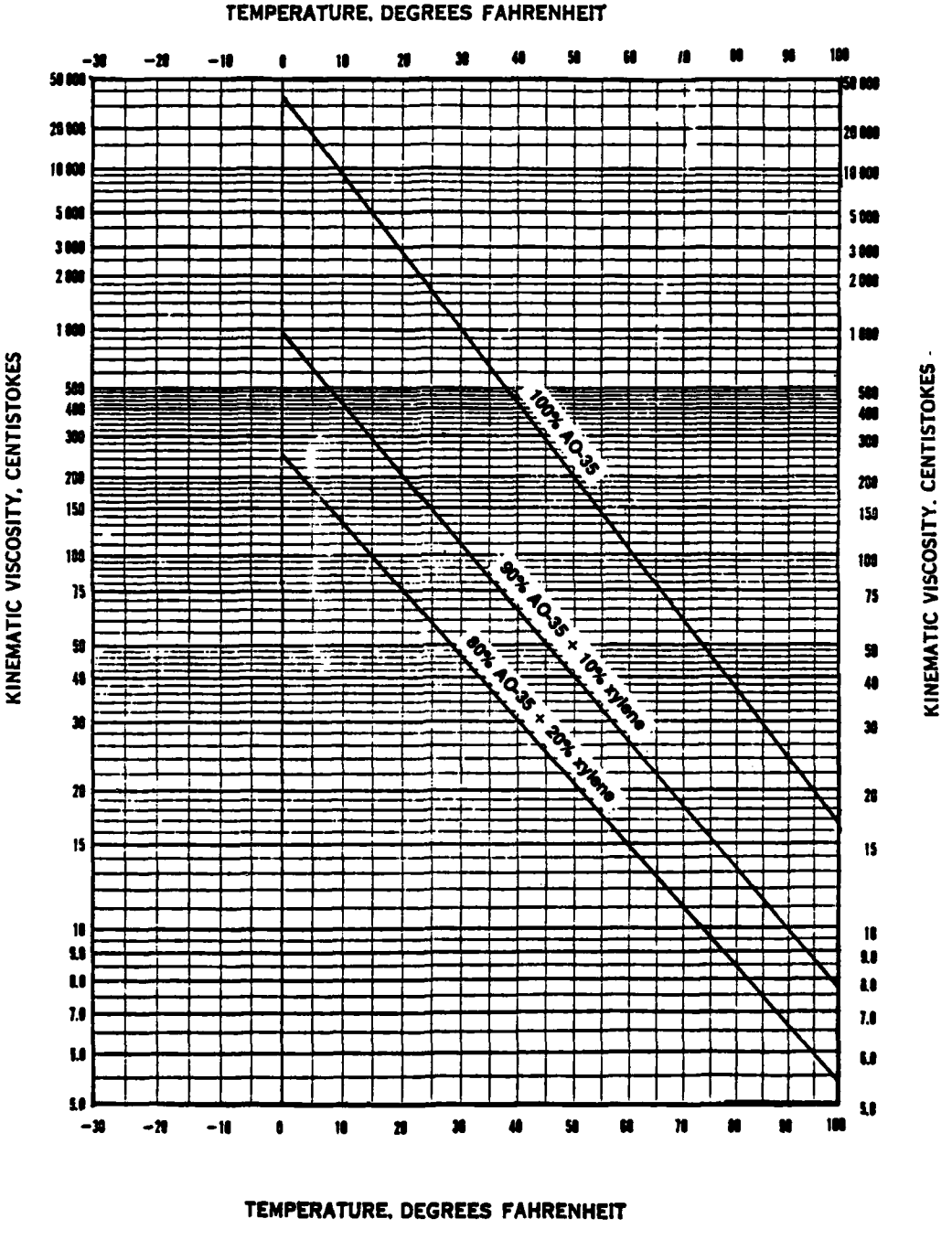
TABLE 6

VISCOSITIES OF AO-35 AND AO-35/XYLENE BLENDS (Weight Basis)

Viscosity @	100% AO-35	90% AO-35 10% Xylene	80% AO-35 20% Xylene
0°F (−18°C) SUS	144,330	4,590	1,150
cSt	31,350	997	250
32°F (0°C) SUS	3,340	448	187
cSt	724	97	40
77°F (25°C) SUS	182	77	55
cSt	39	15	9
100°F (38°C) SUS	84	52	44
cSt	17	7.8	5.4

To prevent partial extraction of the antioxidant by strong caustic solution, AO-35 should be added after caustic scrubber treatment. This precaution should be observed with all alkylated phenols.

FIGURE 1
VISCOSITY OF AO-35 AND AO-35/XYLENE BLENDS



TOXICITY PRECAUTIONS

Precautions in Handling – Causes burns (as defined by D.O.T. Skin Corrosivity Test). Combustible. Do not get in eyes, on skin, on clothing. Avoid breathing vapor. Keep container closed. Use with adequate ventilation. Wash thoroughly after handling. Keep away from heat and flame.

In case of fire, use water spray, foam, dry chemicals or CO_2.

First Aid – In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse.

PACKAGES AND SHIPPING POINTS

The standard package for AO-35 is a non-returnable 55-gallon steel drum containing 419 lb net and having a tare weight of 50 lb. Drum shipments are made from Deepwater, New Jersey, and the following warehouses:

Billings, Montana	Los Angeles, California
Chicago, Illinois	Houston, Texas
Kansas City, Missouri	

Amounts smaller than the standard package are available upon request. Bulk shipments are available by tank car or tank truck from Deepwater, New Jersey.

ADDITIONAL INFORMATION

Additional information and samples may be obtained from any of the sales offices listed on page 7.

Du Pont Petroleum Chemicals
Wilmington, Delaware 19898

UNITED STATES

CENTRAL REGION

- SCHAUMBURG, Illinois 60195 — (312) 982-4173
  1400 North Meacham Road

EASTERN REGION

- WYNNEWOOD, Pennsylvania 19096 — (215) 896-2000
  308 East Lancaster Avenue
- NEW YORK, New York 10001 — (212) 971-4862
  Empire State Building, Room 408

GULF COAST REGION

- HOUSTON, Texas 77002 — (713) 658-1151
  Suite 490, Dresser Tower, 601 Jefferson Street

MID-CONTINENT REGION

- TULSA, Oklahoma 74101 — (918) 583-8581
  P. O. Box 730, 1811 S. Baltimore Avenue

WESTERN REGION

- LOS ANGELES, California 90017 — (213) 624-1354
  Suite 427, 612 South Flower Street
- SAN FRANCISCO, California 94104 — (415) 392-1934
  Room 834, 111 Sutter Street

CANADA

DU PONT OF CANADA LIMITED

- TORONTO, Ontario M5K 1B6 — (416) 362-5621
  P. O. Box 26, Toronto-Dominion Centre
- CALGARY, Alberta T2S 2S5 — (403) 265-9060
  Suite 1500, 1800 Fourth Street, S.W.
- LACHINE, Quebec H8T 2V5 — (514) 636-4580
  1600 50th Avenue

EUROPE

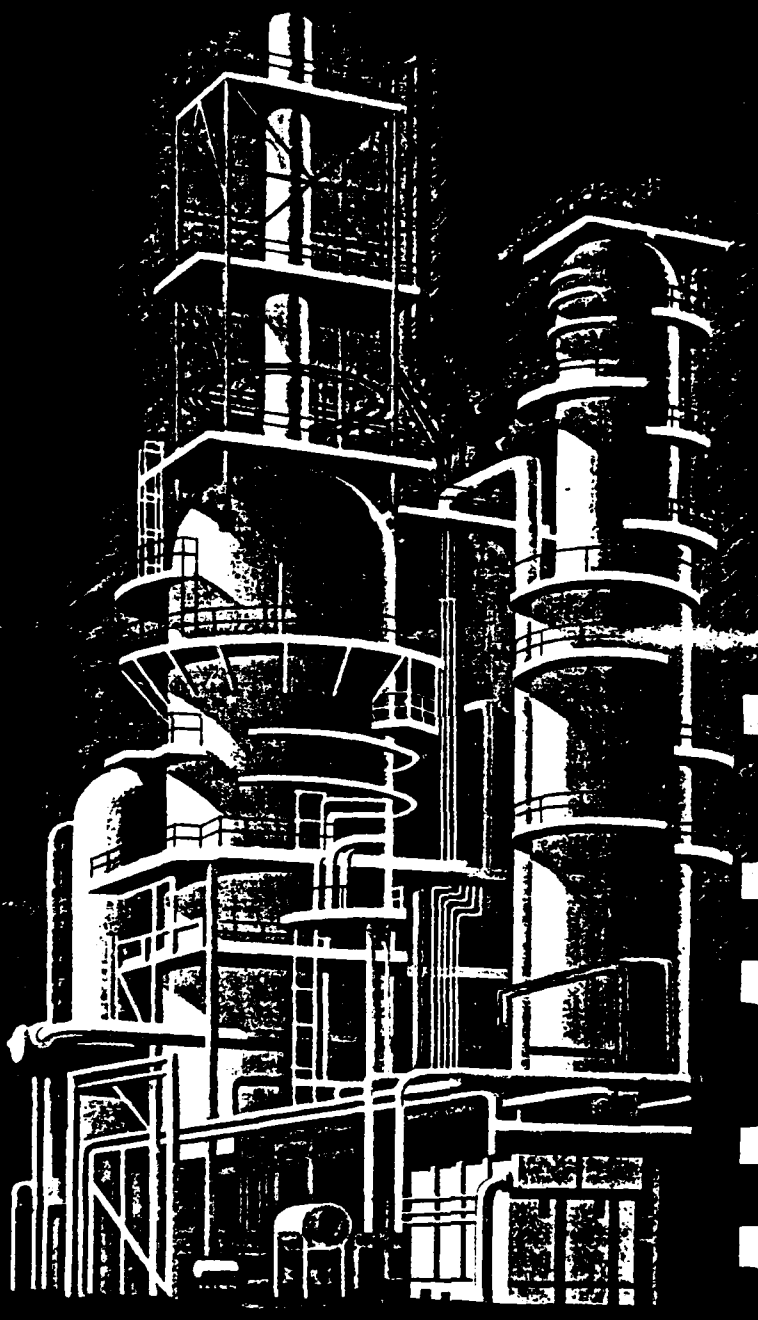
DU PONT DE NEMOURS (BELGIUM)

- B-1000 BRUSSELS, Belgium — (02) 573 74 60
  7, rue Joseph Stevens

OTHER COUNTRIES

INTERNATIONAL MARKETING

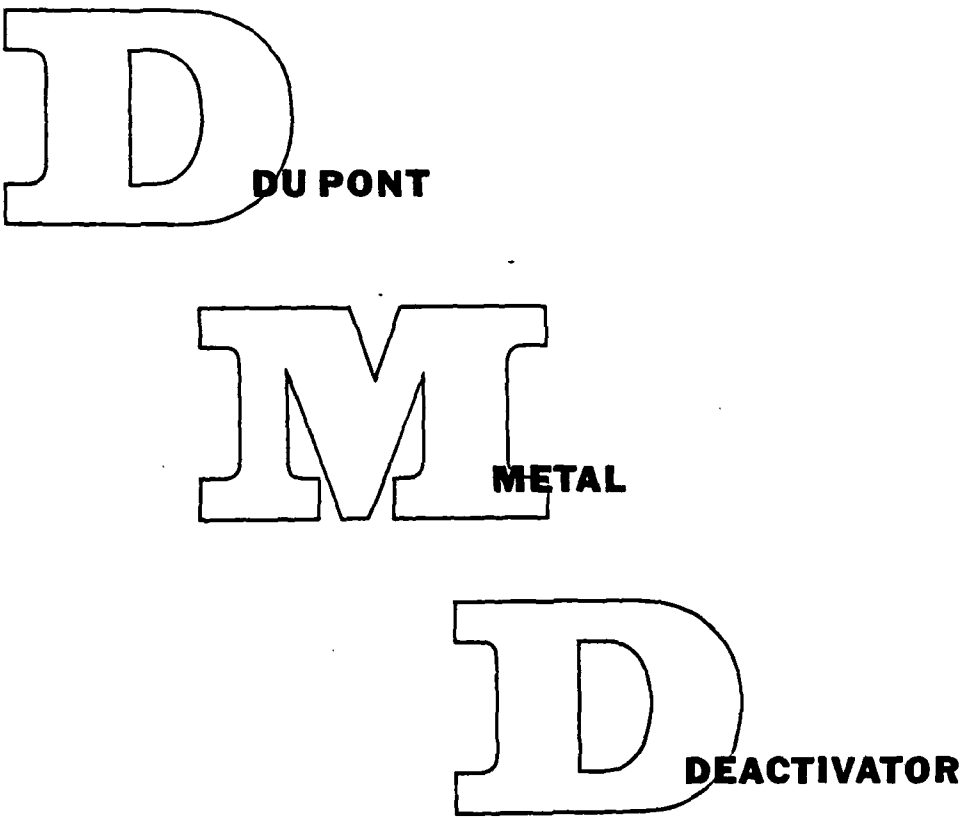
- WILMINGTON, Delaware 19898 — (302) 774-5433



D DU PONT

M METAL

D DEACTIVATOR


D
DU PONT
M
METAL
D
DEACTIVATOR

BACKGROUND

With the increased production of cracked gasolines in the early twenties came the problem of gum formation. This gum formation took place in everything from refinery storage tanks to automobile carburetors. In an effort to control gasoline stability, acid or clay treating was used. These processes are expensive and reduce the yield and octane quality of the finished fuel.

Gasoline antioxidants, developed in the early thirties, provided a means for improving gasoline stability, but for unknown reasons were sometimes ineffective in certain stocks. In 1933, several members of the Du Pont Jackson Laboratory staff met to discuss this problem with representatives of an oil company. From this

meeting came the thought that small amounts of copper in gasoline might be catalyzing the chemical reactions leading to gum formation. Work began immediately on the problem of copper deactivation and several promising additives were synthesized. The original Du Pont offering was N,N'-disalicylidene-1,2-ethanediamine, marketed as Lube Oil Color Stabilizer S. Although this deactivator did an excellent job, it was a solid and difficult to handle. Subsequently, a product was developed with N,N'-disalicylidene-1,2-propanediamine as the active ingredient. This product, Du Pont Metal Deactivator, has done an outstanding job since its introduction in 1939.

Du Pont Metal Deactivator can be used in a wide variety of petroleum products with unique and beneficial results. The benefits of DMD arise from the fact that it improves product stability through deactivation of copper which may enter the product during manufacture, distribution, or use.

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COPPER CATALYSIS AND DEACTIVATION

Copper and many of its compounds are powerful pro-oxidants and, as such, are detrimental in two ways to the quality of petroleum products. First, copper accelerates the rate of oxidation of hydrocarbons by promoting degenerative chain branching. The free radicals, which are developed as shown below, initiate the chain type oxidation and polymerization reactions which lead to gum and sediment formation.

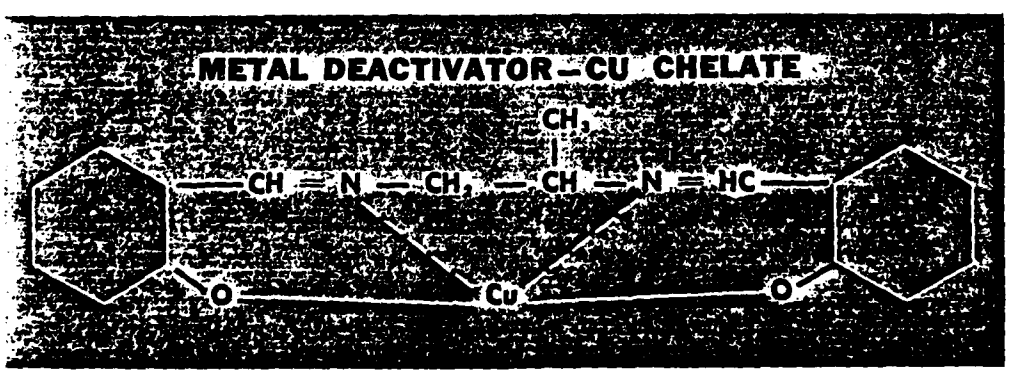
$$Cu + \text{peroxide} \longrightarrow Cu^{++} + \text{chain-initiating free radicals or}$$

$$Cu^{+} + \text{peroxide} \longrightarrow Cu^{++} + \text{chain-initiating free radicals}$$

The second adverse effect of copper is that it may react with antioxidants which are present and reduce or destroy their efficiency, as shown below:

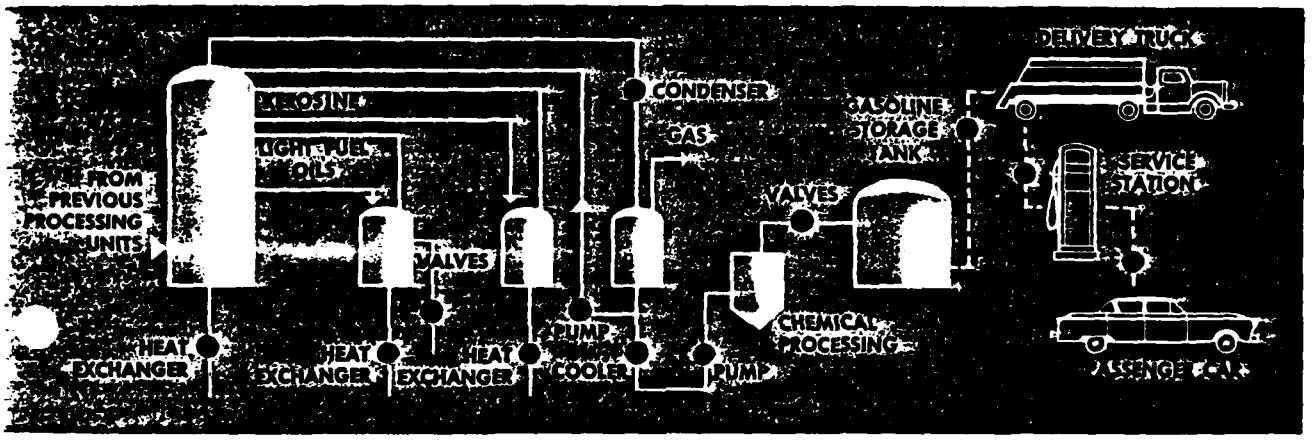
$$Cu^{++} + \underset{\text{(EFFICIENT)}}{\text{antioxidant}} \longrightarrow Cu^{+} + \underset{\text{(LESS EFFICIENT)}}{(\text{antioxidant}-1\ \text{electron})^{+}}$$

Du Pont Metal Deactivator (DMD) prevents these undesirable reactions by combining with dissolved copper to form a stable chelate. In this form the copper is inactive and has no pro-oxidant effect. The chelate is illustrated schematically below:



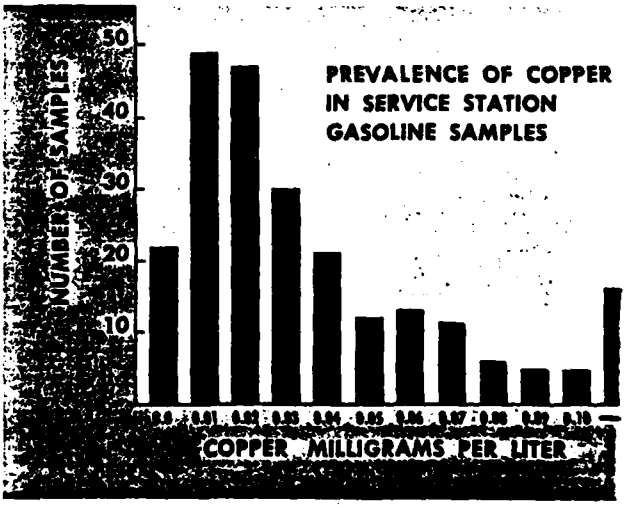
2. SOURCES OF COPPER CONTAMINATION

There is a popular misconception that only products that are copper treated are contaminated with copper and require deactivation. Since as little as 0.007 mg. of copper per liter will exert a harmful pro-oxidant effect, virtually any equipment containing copper or copper alloys is a potential source of trouble. Hydrocarbon-soluble copper compounds are formed by the reaction of copper with phenols or acidic materials such as mercaptans. The following schematic diagram shows some of the possible sources of copper contamination present in a typical refinery.



● These are typical points for copper contamination.

Many additional sources of copper contamination are encountered after the finished product leaves the refinery. Pipelines, distribution terminals, and pumps with their brass filters, copper tubing, and bronze fittings are a further source of contamination. Refiners have no control over these sources. Du Pont Metal Deactivator offers inexpensive protection against such copper contamination and is widely used for this purpose.



In a recent survey of 241 service station samples from 49 cities in the United States and Canada, 91 per cent were found to contain copper ranging up to 0.9 mg. per liter.

APPLICATION

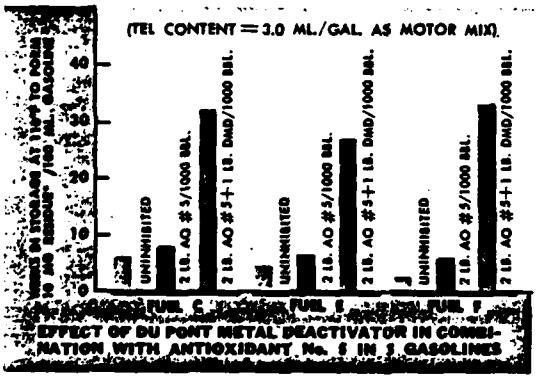
MOTOR GASOLINES

DMD is widely used in motor gasolines because of the outstanding benefits that accrue from its use. In many instances, its use saves the refiner money.

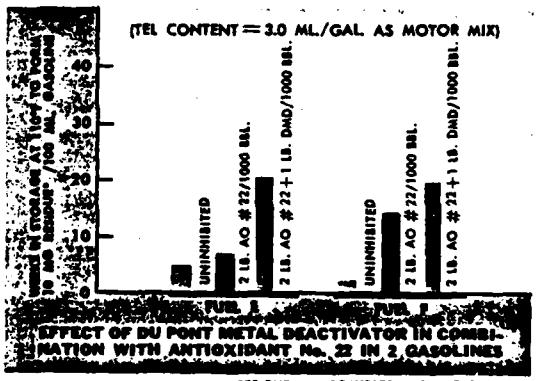
Consider the refiner who desired a gum level of 10 milligrams or less per 100 milliliters after 50 days at 110°F. He was using 12 pounds of Du Pont Gasoline Antioxidant No. 5 per 1000 barrels to obtain this stability level and his treating cost per thousand barrels was $6.72.* This gasoline contained only a trace of copper, but by adding one pound of DMD per thousand barrels he was able to obtain the desired stability level with only three pounds of Antioxidant No. 5 per thousand barrels. The treating cost per thousand barrels was reduced to $3.51.* Thus, this refiner reduced costs and improved product quality, since the amount of DMD used also protected his product to some extent against the effects of additional copper contamination after leaving the refinery.

The cost of producing high octane motor gasolines of good quality is great. The use of DMD at a concentration of 1 pound per 1000 barrels to protect that quality is an inexpensive investment amounting to less than ⅛ of a cent per barrel. Examples of the effect of DMD in increasing the storage stability of typical gasolines are shown below:

**Costs based on prices of Du Pont Gasoline Antioxidant No. 5 and Du Pont Metal Deactivator as of 4/1/54.*



EFFECT OF DU PONT METAL DEACTIVATOR IN COMBINATION WITH ANTIOXIDANT No. 5 IN 3 GASOLINES



EFFECT OF DU PONT METAL DEACTIVATOR IN COMBINATION WITH ANTIOXIDANT No. 22 IN 2 GASOLINES

*RESIDUE = INSOLUBLES + SOLUBLE GUM

COMPOSITION, COPPER CONTENT, AND DEACTIVATOR RESPONSE OF TEST FUELS CITED

FUEL COMPOSITION

	Composition, vol. %		
	Fuel C	Fuel E	Fuel F
Catalytic cracked gasoline	30.0	46.0	75.0
Thermal cracked gasoline	13.4	32.0	5.0
Straight run gasoline	56.6	22.0	—
Natural gasoline and light ends	—	—	17.0
Thermal reformed gasoline	—	—	3.0
Copper content p.p.m. by wt.	0.04	0.03	0.05

INDUCTION PERIOD RESPONSE TO METAL DEACTIVATOR

Metal Deactivator Concentration, wt. %	Induction Period, min.		
	Fuel C	Fuel E	Fuel F
None	1078	404	971
0.0001	1159	398	1036
0.0003	1174	407	1035
0.0005	1171	406	1029
0.0008	1170	401	1030

DMD enables the refiner to avoid costly customer complaints, as well as to save money. In one instance, a refiner who was adding 15 per cent casinghead gasoline to his product encountered an epidemic of complaints, due to stuck intake valves caused by gum in the gasoline. In order to maintain customer confidence, the refiner had to pay for the engine repairs. On investigation, it was found that the casinghead gasoline contained copper, and the complaints were eliminated by using DMD.

Another advantage of Du Pont Metal Deactivator in motor gasoline is its effectiveness in preventing haze formation or precipitation in leaded gasolines. An example of this effect is shown in the following table.

EFFECT OF DMD IN PREVENTING PRECIPITATE FORMATION IN GASOLINE

GASOLINE	ADDITIVE CONCENTRATION LBS./1000 BBLS.		APPEARANCE AFTER 4 WEEKS' STORAGE AT 110°F.
	AO-22*	DMD	
REGULAR GRADE	2	0	MEDIUM PRECIPITATE
REGULAR GRADE	2	½	CLEAR
PREMIUM GRADE	2	0	VERY HEAVY PRECIPITATE
PREMIUM GRADE	2	½	VERY SLIGHT PRECIPITATE

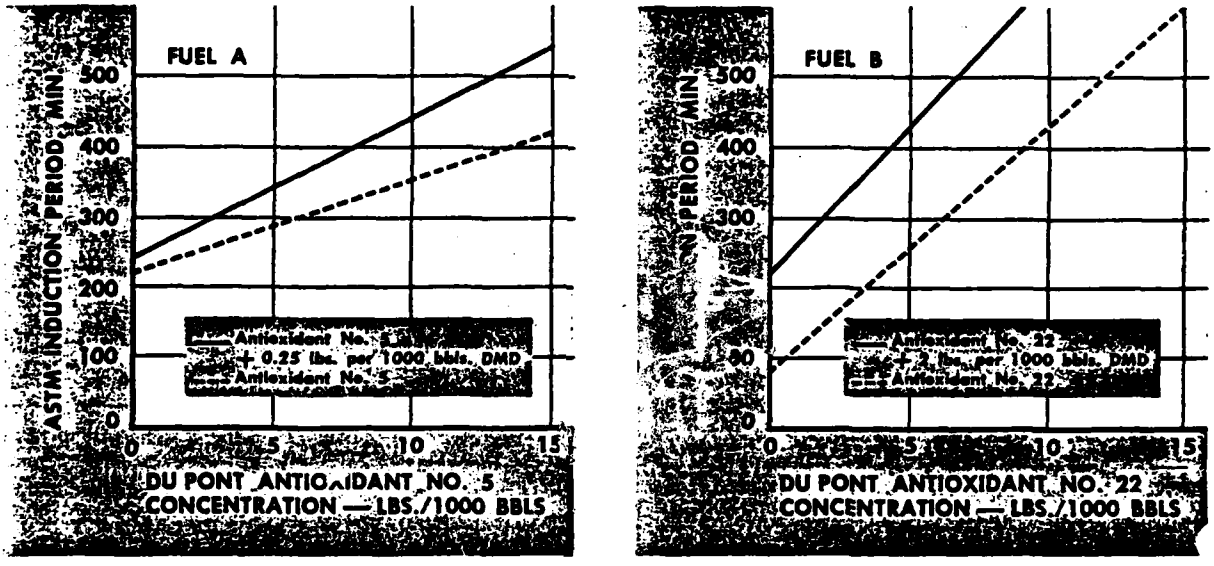
* *Du Pont Gasoline Antioxidant No. 22.*

Deactivator may be used in many stocks to increase ASTM induction period as in Case I, shown below, and in the graphs on page 7.

	ANTIOXIDANT Type	ANTIOXIDANT Lbs/1000 bbl.	DU PONT METAL DEACTIVATOR Lbs/1000 bbl.	A.S.T.M. Ind. Per. Minutes	STORAGE RESULTS 10 mg. gum, days
Case 1	DU PONT No. 5	7.5	0	277	65
	DU PONT No. 5	7.5	1.0	460	225
Case 2	DU PONT No. 5	2	0	404	42
	DU PONT No. 5	2	1.0	406	194

The beneficial effect of DMD in storage is often much greater than would be anticipated on the basis of accelerated test data. This is illustrated in Case 2 on page 6.

EFFECT OF DMD ON ASTM INDUCTION PERIOD



The copper dish gum test is not considered a reliable index of the effectiveness of deactivator, since the large area of copper exposed in the test apparatus tends to nullify the effect of the relatively small concentrations of the additive. However, a beneficial effect is sometimes apparent when DMD is used in higher concentrations with an antioxidant. This effect often enables lower copper dish gum results to be obtained from a combination of deactivator and antioxidant than by the use of either material alone. This effect is shown in the following example:

EFFECT OF ANTIOXIDANT AND DMD ON COPPER DISH GUM

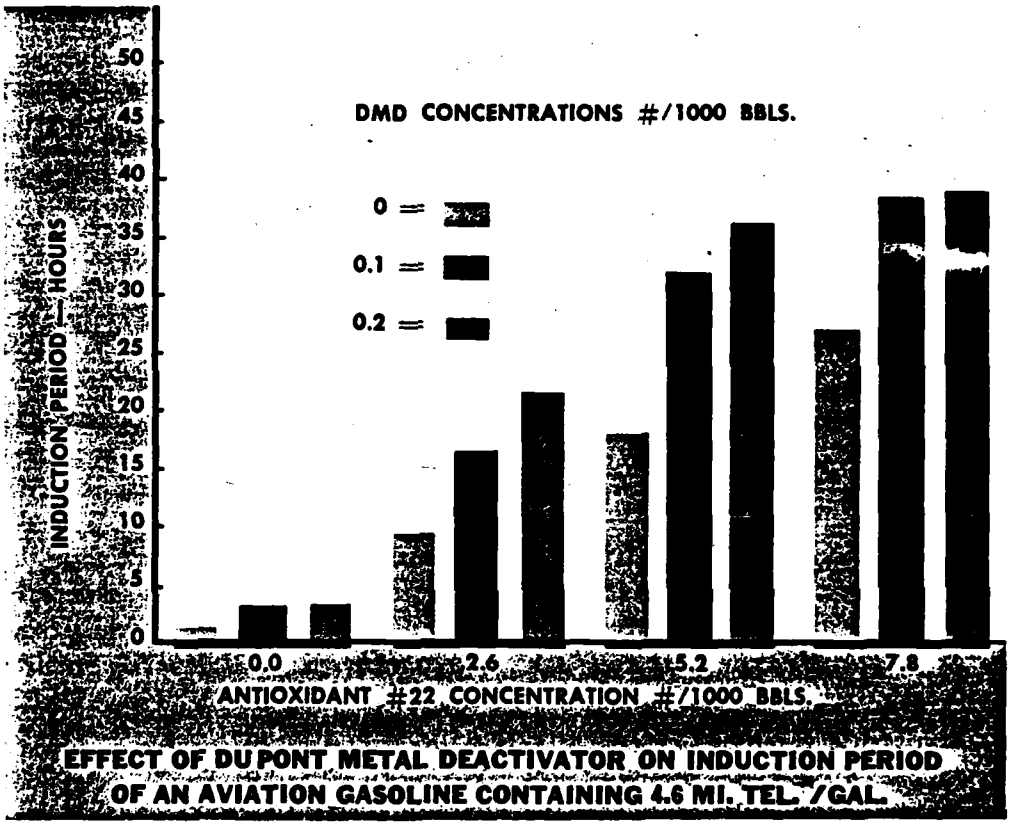
THERMALLY CRACKED GASOLINE		
DMD[1] Wt. %	AO-5[1,2] Wt. %	COPPER DISH GUM, Mg./100 Ml.
—	—	141
0.004	—	90
—	0.010	17
0.004	0.005	11

1—Active Ingredient. 2—Du Pont Gasoline Antioxidant No. 5

AVIATION GASOLINES

DMD has not been approved for use in aviation gasoline. However, its potential usefulness in such products is considerable and may result in its approval at some later date.

In a laboratory study of several aviation gasolines containing less than measurable amounts of copper, it was generally found that supplementing Du Pont Gasoline Antioxidant No. 22 with DMD provided a means of obtaining desired stability at lower cost with less total additive. A typical example of this effect is tabulated below.



EFFECT OF DU PONT METAL DEACTIVATOR ON INDUCTION PERIOD OF AN AVIATION GASOLINE CONTAINING 4.6 ML. TEL. /GAL.

The effect of DMD is even more pronounced in stocks that have been copper sweetened. At times, such stocks cannot meet the storage stability requirements specified for aviation gasolines. Laboratory experiments have demonstrated that the use of small amounts of DMD will usually provide the required stability at lowest cost.

KEROSINES

DMD is used frequently in kerosine and is particularly useful as a color stabilizer in stocks that have been copper sweetened. Dosages range between one-quarter and two pounds per thousand barrels of product. Shown below is an example of the effectiveness of DMD in this application:

KEROSINE		
ADDITIVE	COLOR SAYBOLT	
	ORIGINAL	AFTER 12 WEEKS STORAGE AT 110°F.
NONE	+26	-16
+0.25 LBS. DMD/1000 BBLS.	+26	-26

In addition to its color stabilizing properties, DMD has been found to reduce carbon and coke formation in pot burners by as much as 50 per cent.

JET FUELS

DMD is approved for use in jet fuels in accordance with military jet fuel Specification MIL-F-5624C. This Specification permits the use of a maximum of 2.0 pounds of metal deactivator (active ingredient) per 1,000 barrels of jet fuel.

In a small-scale jet combustion chamber, difficulty with nozzle fouling was experienced when using JP-4 referee fuel. This difficulty manifested itself mainly in relighting. Although the use of Du Pont Fuel Oil Additive No. 2 extended the number of times that the burner could be relighted, the further addition of 2.6 pounds of DMD per thousand barrels eliminated the difficulty.

DIESEL OIL AND HOME HEATING OIL

Du Pont Metal Deactivator is used in many diesel and home heating oils for one or more of the following reasons:

- To prevent color deterioration
- To improve storage stability
- To prevent the formation of copper mercaptide

DMD should not be mistaken for an antioxidant in its application to distillate fuels. Although DMD is of great value when used alone in fuel oils, it is of maximum value when used in combination with an antioxidant and dispersant such as Du Pont Fuel Oil Additive No. 2. DMD is compatible with all known fuel oil additives.

In many fuel oils, DMD will prevent color deterioration caused by copper catalyzed reactions.

It is well known that the most severe conditions of storage occur when a fuel comes in contact with copper or copper and sea water. These conditions are difficult to avoid in the distribution of distillate fuels, but DMD will improve the storage stability of such fuels by combating the harmful effects of copper.

The problem of copper mercaptide formation in diesel and heating oils is serious, since the reaction of the mercaptans with copper or brass can plug filters and stop the flow of oil. This reaction bears no relationship to the stability of the oil. It can occur in a stable oil that does not have a significant amount of insoluble residue, as well as in a less stable oil from which insoluble residue has been removed by a filter. The copper mercaptides appear on the copper or brass parts as white to yellow waxy or jelly-like deposits.

These copper mercaptides are formed through a series of oxidation-reduction reactions in a hydrocarbon system which contains copper or brass, mercaptan, and an oxidized hydrocarbon such as a peroxide. The sequence of the most important reactions is as follows:

1. The oxidation of elemental copper to copper ions by a peroxide.

$$Cu^{\circ} + \begin{matrix} ROOH \\ or \\ ROOR \end{matrix} \longrightarrow Cu^{+} \text{ or } Cu^{++}$$

2. The reaction of copper ions with mercaptans to form copper mercaptide.

$$Cu^{+} + RSH \longrightarrow CuSR + H^{+}$$

$$2Cu^{++} + 4RSH \xrightarrow{\text{or}} 2CuSR + RSSR + 4H^{+}$$

3. The oxidation of mercaptan by a hydroperoxide, catalyzed by copper ions, to form disulfides and reduction products of hydroperoxides.

$$RSH + ROOH \xrightarrow{Cu^{+} \text{ or } Cu^{++}} RS\text{-}SR + \text{other oxidation products such as RCHO, ROH, RCO-R or more complicated sulfur-oxygen compounds.}$$

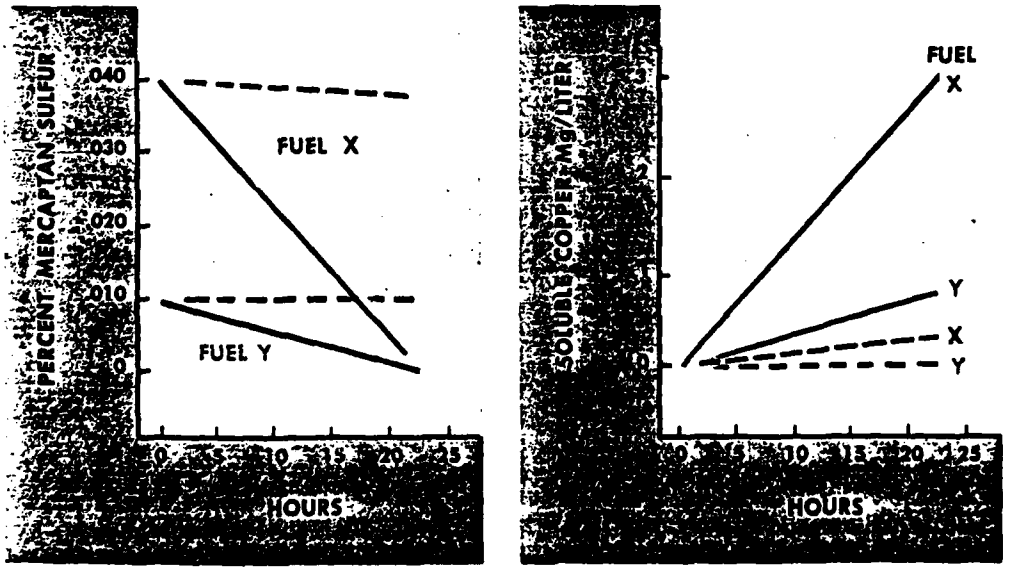
Some mercaptans, such as normal butyl mercaptans, form mercaptides that are insoluble in fuel oil. Others, such as tertiary butyl mercaptan, form mercaptides which are relatively soluble. Therefore, the copper mercaptides either form a residue, which may plug a filter, or provide a means of solubilizing copper. The fuel-soluble copper mercaptides will accelerate the residue-forming reactions of fuel oil.

The reactions listed above can be eliminated by the following procedures:

- Remove or convert the mercaptans.
- Reduce the formation of peroxide by minimizing contact with oxygen.
- Remove sources of, or contact with, copper.
- Add DMD to prevent mercaptide formation.

The first three procedures are all difficult and expensive means for minimizing the deleterious effects of copper and mercaptans. The preferred and economical method for controlling these reactions is to deactivate the copper chemically by using DMD. The treatment is economical and has been accomplished with as little as one-half pound per thousand barrels. The effectiveness of Metal Deactivator in controlling this reaction in the presence of copper is shown below for two concentrations of mercaptan sulfur.

EFFECT OF METAL DEACTIVATOR IN CONTROLLING THE REACTION OF MERCAPTAN AND HYDROPEROXIDE IN PRESENCE OF COPPER



TURBINE OILS

The use of Metal Deactivator in turbine oils is frequently beneficial in actual service; however, this is sometimes difficult to demonstrate in accelerated tests such as ASTM-D-943 "Oxidation Characteristics of Inhibited Steam-Turbine Oils." This is due to the large area of copper wire catalyst used in the test and the long period of the test (1000 hours). The small amounts of DMD normally used in hydrocarbons would be consumed early in the test.

Other additives, such as Du Pont Phenyl-alpha-Naphthylamine and "Ortholeum" 300 Grease Stabilizer, also improve the quality of turbine oil and permit these oils to pass tests such as ASTM-D-943.

GREASES

Du Pont Metal Deactivator has been successfully used in bearing greases. It is frequently combined with an antioxidant such as Phenyl-alpha-Naphthylamine or "Ortholeum" 300 in these applications.

4 SPECIAL APPLICATIONS

DRIVE-AWAY GASOLINE

Drive-away gasoline is a term that refers to gasolines of unusually good storage stability. These contain as much as 12 pounds of Metal Deactivator per 1000 barrels in addition to the normal concentration of a gasoline antioxidant. As the name implies, these gasolines are used for the initial fill of new equipment so that, after extensive storage and transportation, the engines can be operated on the original fill of gasoline without fear of gum trouble.

In certain rare instances, the use of high concentrations of DMD in fuel systems containing copper has resulted in the formation of sufficient quantities of the copper chelate to give the gasolines a green color. If the gasoline is evaporated, the residue may also have the green color of the chelate. This effect, to our knowledge, has never caused any difficulty.

GUM PREVENTIVE COMPOUND

Prior to the use of drive-away gasolines, a mixture known as Gum Preventive Compound was added to the fuel tank at the time of the initial fill or before vehicle storage. The composition was as follows:

4 Ounces (fluid) Solvent—(Benzene, Toluene, or Alcohol)

3 Grams Metal Deactivator*

2 Grams Antioxidant* (AO-5 or AO-22)

*Active Ingredient

The additive concentrate described above was added to tanks containing up to 30 gallons of gasoline, thus providing approximately 10.0 additional pounds of DMD per 1000 barrels and 6.7 pounds of antioxidant.

SWEETENING

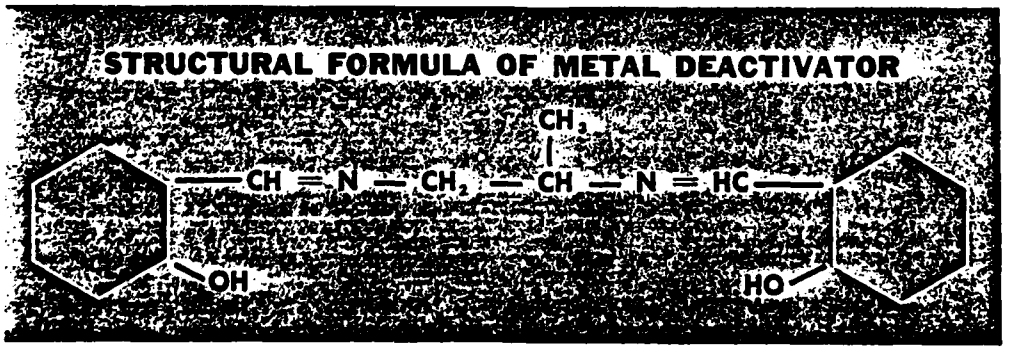
Du Pont Gasoline Antioxidant No. 22 is becoming increasingly popular as a sweetening agent for gasolines. When DMD is used in stocks sweetened by this process, addition should be made after the sweetening has been completed. There are two reasons for this:

1. The strong alkalies used in sweetening may extract a portion of the deactivator.
2. While there are indications that the copper chelate of Metal Deactivator increases the rate of sweetening, uncombined deactivator slows the antioxidant sweetening reaction.

DU PONT METAL DEACTIVATOR: COMPOSITION AND PROPERTIES

CHEMICAL COMPOSITION

DMD is an 80 per cent by weight solution of N,N′-disalicylidene-1,2-propanediamine in an organic solvent. The structural formula of the active constituent is illustrated below:



PHYSICAL PROPERTIES

Du Pont Metal Deactivator is a clear, dark amber liquid with the following typical properties:

SPECIFIC GRAVITY, 60°F./60°F.	1.080
SPECIFIC GRAVITY, 25°C./25°C.	1.075
POUNDS PER GALLON AT 60°F.	9.0
MOLECULAR WEIGHT	282
POUR POINT, °F.	30
VISCOSITY AT 100°F., SUS	115

FLASH POINT, °F.	
(TAG CLOSED CUP)	303
(PENSKY-MARTENS CLOSED CUP)	306
(CLEVELAND OPEN CUP)	325
FIRE POINT, °F.	
(CLEVELAND OPEN CUP)	345

THERMAL DECOMPOSITION

Laboratory tests indicate that the active ingredient of Metal Deactivator is thermally stable at 300°F. Above this temperature, [illegible] At 540°F., the material boils and decomposes rapidly with a rapid darkening in color. The decomposition products are lower-boiling compounds, one of which is phenol.

Generally, chelates are more stable than the constituents from which they are formed and it is believed that the chelates of DMD are more stable than DMD alone.

MISCIBILITY

At temperatures above 10°F., Du Pont Metal Deactivator is miscible in all proportions with benzene and other aromatic solvents, acetone, methanol, xylenols, and Du Pont Gasoline Antioxidants.

It disperses readily in gasolines and distillate oils and is miscible in finished product concentrations at all temperatures. At moderate temperatures, the miscibility of DMD is greater than at low or freezing temperatures. DMD is more soluble in gasolines of high aromatic or olefin content than in straight run or non-olefinic gasolines.

LOW-TEMPERATURE HANDLING

DMD is normally a liquid and can be cooled for a short time to 0°F. without crystallization. However, if crystallization occurs during storage, the product

can be restored to a liquid state without impairing the potency or efficiency of the product by warming to 100°F. or slightly higher. The container should be rolled occasionally to hasten reliquification. Loss of solvent in these operations is not usual, since xylene has a boiling point of 284°F. and a low vapor pressure at 100°F.

EXTRACTION

Refiners may use DMD without fear of extraction by the water bottoms of tanks. DMD is not extracted from gasoline by water solutions having pH values in the range of 4 to 8, even when the gasoline and water solutions are intimately mixed. Approximately 25 per cent of the DMD is extracted by water solutions of pH 10 and 50 per cent at pH 12. DMD is completely extracted by water solutions of pH 2 or below.

Metal Deactivator should not be added prior to treating processes or where there is a possibility of contacting strong bases or acids, since in these instances an appreciable loss of the deactivator would occur.

EFFECT ON ENGINE DEPOSITS

By preventing gum formation, DMD reduces the tendency of fuels to cause deposits in intake systems, combustion chambers, and piston skirts. Normal dosages of DMD in gasoline have no effect on bearing corrosion, as measured in the CRC L-4 engine test.

Intake system deposit tests have been conducted using a single cylinder engine equipped with a glass manifold. Results of these tests indicate that DMD does not increase deposits laid down by a fresh base fuel plus other additives. This is illustrated below:

EFFECT OF DMD ON INTAKE SYSTEM DEPOSITS	AVIATION GASOLINE CONTAINING 4.6 ML TEL/GAL.		
	GLASS MANIFOLD TESTS 0 = CLEAN 300 = DIRTY		
	AO-22 WT. %	DMD WT. %	MANIFOLD RATING*
	0	0	35
	0.0032	0	35-40
	0.0032	0.0006	30-40

* Based on experience a score below 80 indicates a fuel which would be satisfactory in service while fuels believed to cause excessive intake system deposits rate above 120. Fuels rating 80 to 120 are considered borderline.

QUANTITY REQUIRED

The amount of Du Pont Metal Deactivator required in any refinery stream depends on the concentration and nature of the copper present in that stream and on the possibility of copper contamination during the life of the product after it leaves the refinery. Dosages vary from ¼ to 3 pounds of DMD per 1000 barrels.

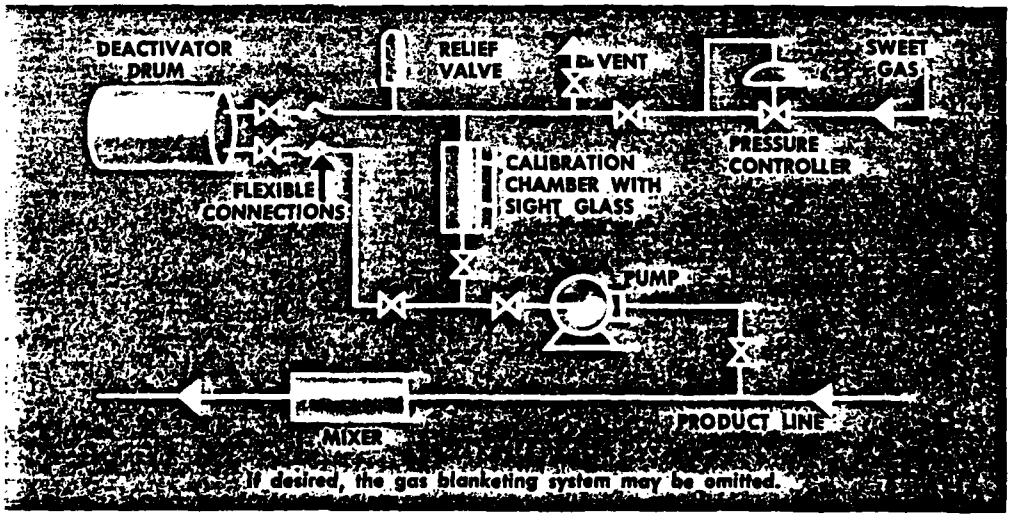
The concentration of DMD required in a gasoline can be calculated stoichiometrically after the copper content of a product has been determined. Practical experience has demonstrated that approximately 1.2 times the stoichiometric concentration is desirable. This concentration can be expressed in common values as follows:

1.0 mg. of copper per liter requires approximately 2.0 pounds of Du Pont Metal Deactivator per 1000 barrels (0.0008 weight per cent)

ADDITION

The concentration of Du Pont Metal Deactivator required is very low; therefore, precautions should be taken to insure thorough mixing. This may be accomplished either by injecting the deactivator continuously into the stream as it is run down or transferred after treating, or by bulk addition with vigorous agitation.

A good method of adding DMD is to pump directly from the container into the stream using a pump capable of accurately injecting small quantities. A sketch of such a system is shown in the figure below:



When deactivator was first used, stock solutions were required to increase the volume of solution and compensate for the lack of a precision pump.

Present-day pumps[1] are capable of accurately injecting less than one pound or less of DMD per day using the principle of differential pumping.[2] Steel tubing and piping are recommended for transferring DMD; copper tubing is not recommended.

In many instances where both DMD and an antioxidant are added, it is possible to combine the antioxidant and deactivator in proper ratio and use only one proportioning pump. If the two are added separately after sweetening operations, the most efficient results can be secured by adding the deactivator before the antioxidant.

Although injection of the deactivator "as received" is generally satisfactory, many refiners use a stock solution. In instances where stock solutions are employed, a cracked gasoline and additional aromatic solvent such as benzene, xylene, or toluene should be used to increase the solubility of the deactivator. The stock solution should be stored at temperatures above 70°F.

(1) Among the equipment manufacturers offering suitable injection pumps are: Zenith Products Co., 58 Chestnut St., West Newton 65, Mass.; %Proportioneers%, Inc., 344 Harris Ave., Providence 1, R.I.; Hills-McCanna Co., 3025 North Western Ave., Chicago 18, Ill.; Milton Roy Co., 1300 East Mermaid Lane, Phila. 18, Pa.; Walter H. Eagan Co., Inc., 2336 Fairmount Ave., Phila. 30, Pa.; Mangel, Inc., 315 Babcock St., Buffalo 10, N. Y.

(2) Differential pumping involves the use of two pumps. The first pump takes suction from the DMD drum and discharges to a "T" fitting. One side of the "T" is connected to the product run-down line. The other is connected with the suction of the second pump. The second pump discharges to the supply or suction line of the first pump. The differential between the capacities of the two pumps is metered through the "T." This system, where pump sizes and speeds may be selected, allows almost any variation in a low range with excellent results.

G ANALYTICAL

In problems dealing with copper contamination and deactivation, it is frequently necessary to determine the concentration of copper present. Du Pont Petroleum Laboratory Method G2, which is a colorimetric procedure utilizing sodium diethyldithiocarbamate reagent, is an accurate and moderately rapid procedure for copper determination in gasoline. Copies of this procedure are available from the Du Pont regional offices or laboratories.

Another useful analytical procedure is Du Pont Petroleum Laboratory Method G37 for determining the amount of uncombined deactivator in a gasoline. This procedure is useful in assisting refiners in determining their margin of safety as supplied by excess deactivator. Copies of this analytical procedure, which involves the use of an ultraviolet spectrophotometer, also are available upon request. While both of these methods are quantitative, they can be readily modified for qualitative determinations.

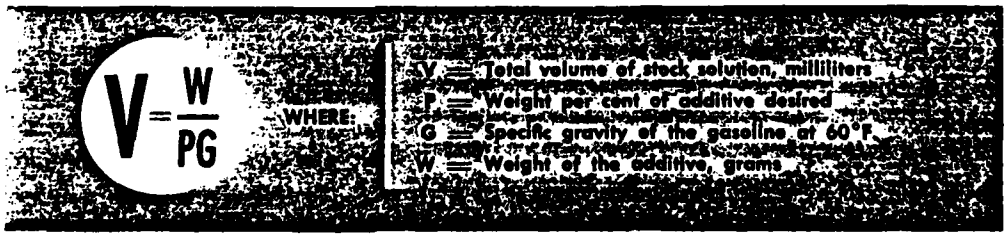
In certain instances, refiners are faced with a situation wherein an unknown quantity of deactivator has been added to a gasoline. The refiner would like to know if all of the copper present has been chelated and, if not, how much additional deactivator is needed. This can be determined in two ways.

The first method would be to determine if there is any uncombined deactivator present by means of Du Pont Petroleum Laboratory Method G37. If not, then incremental concentrations of DMD should be added to the gasoline until analysis shows the presence of sufficient uncombined DMD to indicate the desired margin of safety against copper contamination in the field.

The second method uses the induction period of a gasoline. Incremental concentrations of DMD are added to the gasoline until there is no further increase in induction period. An excess concentration of deactivator can be determined by adding small concentrations of copper until there is a decided decrease in the induction period. To assure consistent and reproducible results, it is important that the copper solution be free from inorganic copper and traces of other metals. After examining and evaluating many organic copper compounds, the Du Pont Petroleum Laboratories have standardized on the use of cupric 2-ethyl hexoate ($C_{16}H_{30}O_4Cu$) dissolved in acetone. The effects of copper contamination and response to Du Pont Metal Deactivator are generally more pronounced in the presence of antioxidants.

Because of the precision necessary in accurately measuring the small quantities of deactivator required to inhibit laboratory test samples, it is advisable to prepare dilute stock solutions in an inert solvent such as anhydrous C.P. benzene and to transfer the requisite volume of these solutions to the gasoline samples by means of a pipette. DMD is quite viscous and it is recommended that it be measured gravimetrically rather than volumetrically.

The volume for diluting a given weight of the additive to obtain the desired concentration when 1 ml. of the stock solution is added to 100 ml. of gasoline can be calculated as follows:



In order to insure that the volume of stock solution (V) is within practical limits, the following table lists the approximate amounts of DMD required for various concentrations:

RECOMMENDED AMOUNTS OF DMD FOR USE IN LABORATORY STOCK SOLUTIONS

METAL DEACTIVATOR DESIRED IN GASOLINE		APPROXIMATE AMOUNT
WEIGHT PER CENT	POUNDS PER 1000 BBLS	OF DMD, ML.
0.0001	0.25	0.02—0.03
0.0002	0.50	0.02—0.03
0.0005	1.25	0.05
0.0010	2.50	0.10
0.0020	5.00	0.20
0.0050	12.50	0.50

* *Assuming gasoline weighing 250 pounds per barrel.*

EXAMPLE:

P=concentration desired—0.0001 weight per cent
G=specific gravity of gasoline—0.7146 at 60°F.
W=weight of approximately 0.02 ml. of deactivator—0.0216 g.

$$V = \frac{W}{PG} = \frac{0.0216}{0.0001 \times 0.7146} = 302 \text{ ml.}$$

The addition of 1 ml. of the stock solution to 100 ml. of gasoline will provide a DMD concentration of 0.0001 weight per cent.

7 GENERAL

PRECAUTIONS IN HANDLING

Skin tests on animals indicate that Du Pont Metal Deactivator can cause skin sensitization. In case of accidental skin contact, wash off immediately with plenty of soap and water. Contaminated clothing should be laundered before re-use.

Since Du Pont Metal Deactivator contains xylene, it should not be stored or handled near an open flame.

PACKAGES

The standard package for Du Pont Metal Deactivator is a non-returnable, synthetazine lined steel drum of 30 gallons nominal capacity. The net weight of each standard package is 260 pounds and the tare weight is 30 pounds.

Smaller quantities of deactivator are available upon request.

SHIPPING POINTS

Stocks of Du Pont Metal Deactivator are maintained at the following convenient locations:

Carney's Point, New Jersey
Chicago, Illinois
Houston, Texas
Los Angeles, California
Tulsa, Oklahoma

From these locations rapid deliveries can be made to all refinery locations.

DU PONT

METAL

DEACTIVATOR

DU PONT

PETROLEUM CHEMICALS DIVISION

Regional Offices

EASTERN REGION
1810 The Americas Building
1270 Avenue of the Americas
New York 20, New York
COlumbus 5-3620; LOngacre 3-6400

MID-CONTINENT REGION
1811 South Baltimore Avenue
Tulsa 14, Oklahoma
Tulsa 5-5578

CENTRAL REGION
8 South Michigan Boulevard
Chicago 3, Illinois
RAndolph 6-8630
ANdover 3-7000, Ext. 289

GULF COAST REGION
705-709 Bank of Commerce Bldg.
Houston 2, Texas
PReston 2857; CHarter 0401

WEST COAST REGION
Suite 560
612 South Flower Street
Los Angeles 17, California
MAdison 5-1691

EXPORT
Petroleum Chemicals Export
Nemours Building, 6539
Wilmington 98, Delaware

IN CANADA
Du Pont Company of Canada Limited
Petroleum Chemicals Division
80 Richmond Street West,
Toronto 1, Ontario

DUPONT

Petroleum Chemicals

DCI-4A

DCI-4A
corrosion inhibitor

DCI-4A is an effective corrosion inhibitor for aviation and motor gasolines and for turbine, jet and other distillate fuels. It protects metal surfaces contacted by these fuels during transfer and storage when used at concentrations ranging from 1 to 8 lbs/1000 bbl (4-32 ppm).

DCI-4A is approved under Military specification MIL-I-25017C for fuel soluble corrosion inhibitors over a concentration range of 2 to 8 lb/1000 bbl (8 to 32 ppm). Under this specification, the relative effective concentration (REC) is 2 lb/1000 bbl (8ppm), the minimum effective concentration (MEC) is 3 lb/1000 bbl (12 ppm), and the maximum allowable concentration (MAC) is 8 lb/1000 bbl (32 ppm). DCI-4A also has been approved for use in fuels meeting the following Military and Federal specifications:

MIL-T-5624K	-	Turbine Fuel, Grades JP-4 and JP-5
MIL-T-83133	-	Jet Fuel, Grade JP-8
MIL-T-25524B	-	Turbine and Jet Engine Fuel, Thermally Stable
MIL-G-3056D	-	Gasoline, Automotive, Combat
VV-G-76B	-	Gasoline, Automotive
VV-G-001690A	-	Gasoline, Automotive, Low Leaded or Unleaded

DCI-4A is also approved for use in the following turbine fuels:

General Electric Co.	D50TF2-S5
Pratt & Whitney Aircraft	PWA 522-J, PWA 523-E & PWA 535
Detroit Diesel - Allison	EMS-64H
Rolls Royce (Fuels for engines RB211, 22B, 524, and 524B)	
Civilian Aviation Authority, England	
Ministry of Defense, England	DERD 2461

COMPOSITION AND PROPERTIES

DCI-4A is a clear, dark amber colored liquid containing only carbon, hydrogen and oxygen in its formulation. The following properties are typical:

Specific Gravity, 60/60 F (15.6/15.6C)			0.94
Density, lb/gal, 60 F (15.6C)			7.8
Pour Point			-65 F (-54C)
Viscosity: (See Fig. 1)	Temperature	SUS	cSt
	210 F (99C)	56.1	9.1
	100 F (38C)	270	58.2
	32 F (0C)	2053	445
Flash Point, Pensky-Martens Closed Cup			89 F (31.7C)
Ash Content, Wt%			0.00
Solubility in Hydrocarbons			Completely Miscible

CORROSION INHIBITION

As indicated in Table I, DCI-4A provides excellent rust protection in hydrocarbon systems as manifested by results obtained using the National Association of Corrosion Engineers, NACE TM-01-72 rust test; Military specification MIL-I-25017C rust test; and ASTM D 665A rust test.

TABLE I

CORROSION INHIBITING PERFORMANCE OF DCI-4A

Rust Test	lb DCI-4A/1000 bbl Required to Pass Rust Test*			
	JP-4	Motor Gasoline	Diesel Fuel	Fuel Oil
NACE TM-01-72(1) 100 F, 3-1/2 hr, distilled finish	1	3	1	3
MIL-I-25017C(2) 100 F, 5 hr, medium hard water, 400 grit mirror finish	2	3	3	3
ASTM D 665A(3) 100 F, 20 hr, distilled water, 240 grit mirror finish	2	3	3	4

Rating Systems

(1) Pass - B+ rating or better (less than 5% rust)

Fail - B rating or poorer (5% or more rust)

(2) Pass - 5 or less rust spots on center 1-7/8" section of billet.

Fail - More than 5 rust spots or 1 rust spot greater than 1 mm in diameter.

(3) Pass - Light rust (less than 6 rust spots)

Fail - Moderate or heavy rust (6 or more rust spots)

* All untreated fuels failed rust tests with 90 - 95% rust.

WATER TOLERANCE AND SEPAROMETER TESTS

At normal use concentrations DCI-4A does not significantly affect the water retention properties of jet fuels as measured by ASTM Method D 2550, Water Separation Characteristics of Aviation Turbine Fuels (Table II). Also, DCI-4A does not appear to cause an inter-reaction between fuels and water as measured by ASTM Method D 1094-72, Water Reaction of Aviation Fuels (Table III).

TABLE II

DCI-4A DOES NOT SIGNIFICANTLY AFFECT
WATER RETENTION PROPERTIES - ASTM D 2550

Fuels	DCI-4A Conc., lb/1000 bbl	WSIM Rating
Bayol R-34/Toluene, 85/15 [illegible] (1)	0	98
	[illegible]	[illegible]
	6	86
JP-4	0	78
	8	81

(1) MIL-I-25017C reference fuel. Rating of 70 or greater is passing.

TABLE III

DCI-4A DOES NOT CAUSE WATER INTER-REACTION OF FUELS

Fuels	DCI-4A Conc., lb/1000 bbl	Water Rating*
JP-4	0	1b
	8	1b
JP-5	0	1b
	8	1b
Commercial Motor Gasoline	0	1
	8	1b
Isooctane	0	1
	8	1

*Values of 2 or greater are usually considered unsatisfactory.

COMPATIBILITY WITH OTHER ADDITIVES

DCI-4A is compatible with all fuel soluble corrosion inhibitors on the Qualified Products List (QPL) of specification MIL-I-25017C. No visual evidence of precipitation or cloudiness occurs when JP-4 fuel containing the maximum allowable concentration of 8 lb DCI-4A/1000 bbl is mixed with an equal volume of JP-4 containing the other approved inhibitors at their maximum allowable concentration.

DCI-4A is compatible with other commonly used fuel additives including antioxidants metal deactivators, metal suppressors, gasoline multifunctional additives, fuel oil additives and rust inhibitors.

DCI-4A IS ESPECIALLY EFFECTIVE IN JET FUELS

DCI-4A is especially cost effective in jet fuel because of its corrosion inhibiting performance and its excellent lubricity characteristics. DCI-4A has a minimal effect on WSIM performance when used either alone or in combination with other additives required in jet fuel.

Test with DCI-4A in JP-5 Jet Fuel have shown a 50% reduction in the coefficient of friction when the additive was evaluated at 7.5 lb/1000 bbl (30 ppm). In another study DCI-4A was found to be highly effective in imparting lubricity to JP-4 Jet Fuel.

STORAGE STABILITY

DCI-4A is not affected by storage temperatures as high as 150 F (65C) for prolonged periods of time. Samples of DCI-4A which had been stored at a temperature of 150 F showed no visual evidence of cloudiness or precipitation, nor were the antirust and water contact properties of DCI-4A affected by storage conditions.

HANDLING PROPERTIES

DCI-4A may be unloaded satisfactorily without heating at temperatures as low as 30 F (-1C). Heating DCI-4A for purposes of accurate metering should not be required at temperatures as low as 0 F (-18C). The handling characteristics of DCI-4A as a function of viscosity versus temperature are shown in Figure 1.

PRECAUTIONS IN HANDLING

Flammable. Causes irritation. Keep away from heat, sparks and open flame. Keep container closed. Use with adequate ventilation. Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.

In case of fire, use water spray, foam, dry chemical or CO_2.

FIRST AID

In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician. Wash skin with soap and water.

PACKAGES AND SHIPPING POINTS

The standard package for DCI-4A is a non-returnable 55-gallon (208 - liter) steel drum containing 419 lb (190 kg) net and having a tare weight of 50 lb (22.7 kg). Drum shipments are made from Deepwater, New Jersey, and the following warehouses:

Billings, Montana	Houston, Texas
Berlin, Illinois	Kansas City, Missouri
Des Plaines, Illinois	Los Angeles, California

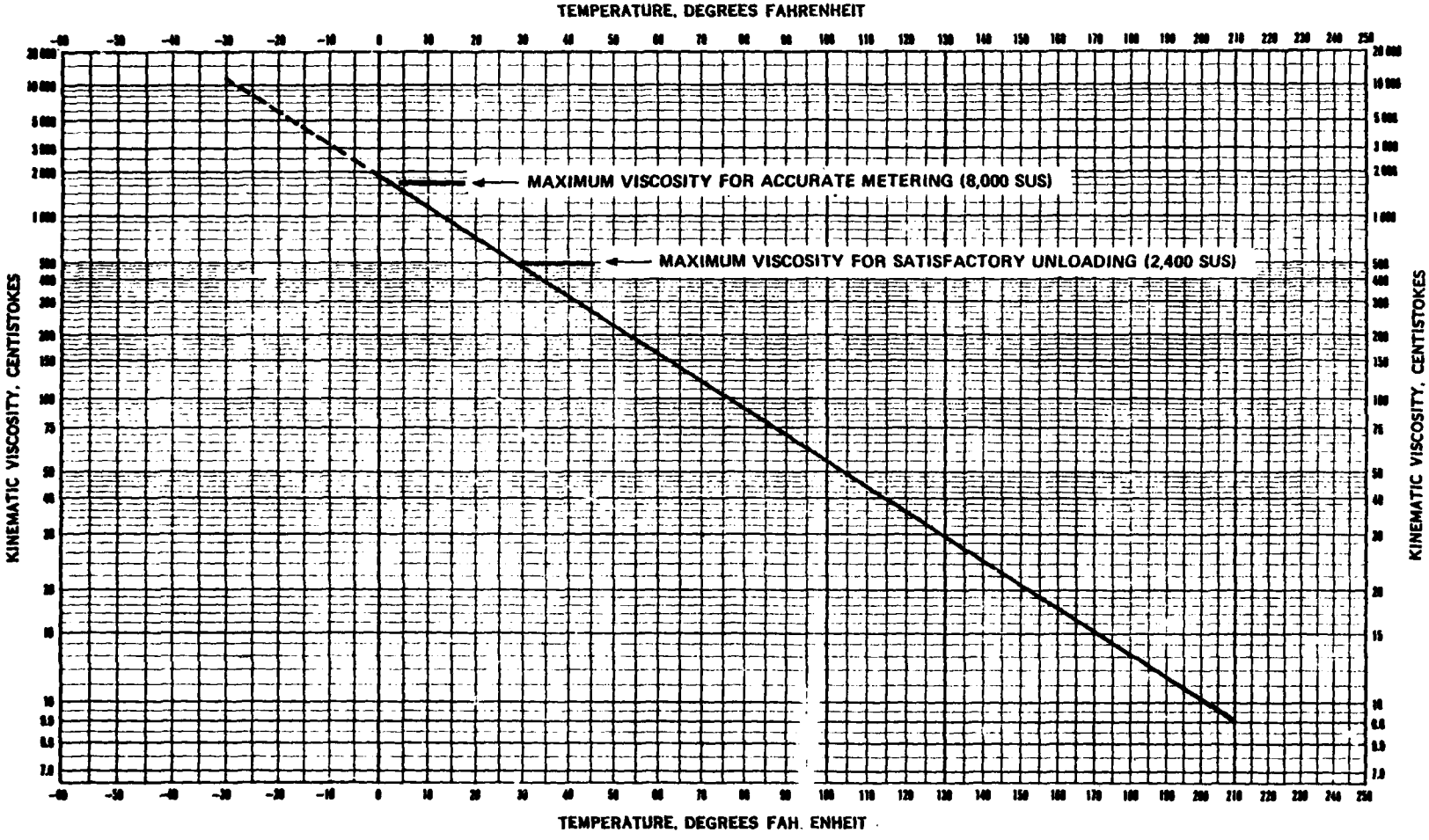
Amounts smaller than the standard package are available upon request. Bulk shipments are available by tank car or tank truck from Deepwater, New Jersey.

ADDITIONAL INFORMATION

Additional information and samples can be obtained from any of the Du Pont Petroleum Chemicals Division offices listed on page 7.

Figure 1

VISCOSITY AND HANDLING CHARACTERISTICS OF DCI-4A



Du Pont Petroleum Chemicals
Wilmington, Delaware 19898

UNITED STATES

CENTRAL REGION

- SCHAUMBURG, Illinois 60195 — (312) 982-4173
  1400 North Meacham Road

EASTERN REGION

- WYNNEWOOD, Pennsylvania 19096 — (215) 896-2000
  308 East Lancaster Avenue
- NEW YORK, New York 10001 — (212) 971-4862
  Empire State Building, Room 408

GULF COAST REGION

- HOUSTON, Texas 77002 — (713) 658-1151
  Suite 490, Dresser Tower, 601 Jefferson Street

MID-CONTINENT REGION

- TULSA, Oklahoma 74101 — (918) 583-8581
  P. O. Box 730, 1811 S. Baltimore Avenue

WESTERN REGION

- LOS ANGELES, California 90017 — (213) 624-1354
  Suite 427, 612 South Flower Street
- SAN FRANCISCO, California 94104 — (415) 392-1934
  Room 834, 111 Sutter Street

CANADA

DU PONT OF CANADA LIMITED

- TORONTO, Ontario M5K 1B6 — (416) 362-5621
  P. O. Box 26, Toronto-Dominion Centre
- CALGARY, Alberta T2S 2S5 — (403) 265-9060
  Suite 1500, 1800 Fourth Street, S. W.
- LACHINE, Quebec H8T 2V5 — (514) 636-4580
  1600 50th Avenue

EUROPE

DU PONT DE NEMOURS (BELGIUM)

- B-1170 BRUSSELS, Belgium — (02) 673.99-16
  150, Chaussee de la Hulpe/Box 16

OTHER COUNTRIES

INTERNATIONAL MARKETING

- WILMINGTON, Delaware 19898 — (302) 774-5433

DUPONT

Petroleum Chemicals

DCI-6P

DCI-6A
corrosion inhibitor

DCI-6A is an effective corrosion inhibitor for motor gasolines, jet fuels and other distillate products. It provides excellent protection against corrosion during pipeline transfer and storage of these products. It protects metal surfaces contacted by these fuels during transfer and storage when used at concentrations ranging from 1 to 10 lb/1000 bbl (4 to 40 ppm).

DCI-6A is approved under Military specification MIL-I-25017C for fuel soluble corrosion inhibitors. Under this specification, the relative effective concentration (REC) is 2 lb/1000 bbl (8 ppm), the minimum effective concentration (MEC) is 3 lb/1000 bbl (12 ppm), and the maximum allowable concentration (MAC) is 8 lb/1000 bbl (32 ppm). DCI-6A also has been approved for use in fuels meeting the following Military and Federal specifications:

MIL-T-5624	-	Turbine Fuel, Grades JP-4 and JP-5
MIL-G-3056	-	Gasoline, Automotive, Combat
VV-G-76	-	Gasoline, Automotive
VV-G-001690	-	Gasoline, Automotive, Low Leaded or Unleaded
VV-F-800	-	Diesel Fuels

COMPOSITION AND PROPERTIES

DCI-6A is a clear, dark amber liquid containing only carbon, hydrogen, and oxygen in its formulation. The following properties are typical:

Density at 60 F (16 C)
- g/ml 0.93
- lb/gal 7.8

Pour Point ..... below -60 F (-51 C)
Flash Point, (Pensky-Martens Closed Cup) ..... 94 F (34 C)
Ash Content, wt% 0.0
Solubility in Hydrocarbons ..... Completely Miscible
Viscosity:

Temperature	SUS	cSt
32 F (0C)	2104	456
100 F (38C)	233	50
210 F (99C)	52	8

CORROSION INHIBITION

DCI-6A provides excellent rust protection at low treating levels in a wide variety of fuels including leaded and unleaded gasolines, kerosine, jet fuels, and other distillate products. Because of higher energy costs to pump liquids through rusted pipe as well as high investments associated with pipelines and other product handling facilities, many shippers rely on inhibitors to provide rust-free protection for fuels. DCI-6A imparts this high degree of rust protection at low dosage levels. Usually "A" ratings* are obtained at less than 2.0 lb/1000 bbl (8 ppm). Even lower inhibitor levels are satisfactory if performance standards such as a "B+" rating by the NACE test are acceptable. Table I below illustrates the DCI-6A concentrations to achieve "A" ratings in a wide variety of commercial fuels:

TABLE I
DCI-6A IS EFFECTIVE AT LOW
CONCENTRATIONS IN A WIDE RANGE OF FUELS

	NACE Rust Test Rating*					
	No	DCI-6A, lb/1000 bbl				
Fuel	Additive	0.6	0.8	1.1	1.7	2.2
Leaded Regular Gasoline	C	A				
[illegible]						
Leaded Regular Gasoline	C	A				
Leaded Premium Gasoline	C	-	-	A		
Unleaded Regular Gasoline	D	A				
Unleaded Regular Gasoline	B	A				
Leaded Regular Gasoline +10% Ethanol	C	-	-	A		
Leaded Regular Gasoline +5% t-Butanol	E	-	-	B	-	A
JP-4 Jet Fuel	E	-	-	B++	-	A
JP-4 Jet Fuel	E	-	-	B	B++	A
JP-4 Jet Fuel	E	-	B++	A		
Jet A Fuel	B	-	-	A		
Kerosine	D	-	-	A		
Grade No. 1 Diesel Fuel	D	-	B	A		
Grade No. 2 Diesel Fuel	D	-	A			
Grade No. 2 Fuel Oil	C	-	-	B+	A	

*National Association of Corrosion Engineers, NACE TM-01-72 rust test. Test conditions 100 F, 3-1/2 hours, distilled water, 100 grit cross hatch finish.

Rating	Proportion of Test Surface Rusted
A	None
B++	Less than 0.1% (2 or 3 spots of no more than 1mm diameter)
B+	Less than 5%
B	5 to 25%
C	25 to 50%
D	50 to 75%
E	75 to 100%

The performance of DCI-6A is outstanding when compared to other leading inhibitors. This performance is summarized in Table II. The competitive corrosion inhibitors, labeled as "CI- ", are materials qualified under QPL-25017-11.

TABLE II
COMPARISON OF DCI-6A & COMPETITIVE INHIBITORS

Additive	Additive Levels (lb/1000 bbl) Required to Obtain Rust Free "A" Ratings by NACE TM-01-72 Test*		
	Regular Gasoline*	JP-4 Jet Fuel*	No. 2 Fuel Oil*
DCI-6A	1	1	3
CI-24	3	4	4
CI-76	6	3	7
CI-81	2	4	5
CI-99	4	3	6
CI-105	4	4	9
CI-106	5	5	6
CI-107	3	2	7
CI-109	6	5	6
CI-114	4	4	4
CI-115	6	5	7
CI-116	6	6	8

*Regular grade gasoline and JP-4 jet fuel had "E" ratings before inhibitor addition. The No. 2 Fuel Oil had a "D" rating before inhibitor addition.

WATER TOLERANCE AND WATER SEPAROMETER TESTS

At normal use concentrations, DCI-6A does not affect significantly the water separometer ratings of jet fuels as measured by ASTM Method D-2550 and has only a modest effect at 8 lb/1000 bbl (32 ppm), the maximum allowable concentration under MIL-I-25017C (Table III). Further, DCI-6A does not cause an interaction between fuels and water as measured by ASTM Method D-1094-72, Water Reaction of Aviation Fuel (Table III).

TABLE III
DCI-6A DOES NOT SIGNIFICANTLY AFFECT
WATER RETENTION PROPERTIES (ASTM-D-2550) OR
WATER INTERACTION PROPERTIES (ASTM-D-1094-72) OF FUELS

Fuel	DCI-6A Conc., Lb/1000 Bbl.	ASTM-D-2550 WSIM Rating (1)	ASTM-D-1094-72 Water Rating (2)
JP-4	0	100	1
	3	[illegible]	[illegible]
	8	82	1
Jet A	0	95	1
	3	89	1
	8	83	1

(1) Water Separation Index, Modified (WSIM) rating of 70 or greater is passing.

(2) Values of 1 and lb are considered satisfactory.

THERMAL OXIDATION STABILITY TEST (JFTOT)

DCI-6A does not affect the thermal stability of jet fuels as measured by the Thermal Oxidation Stability Test (JFTOT) ASTM-D-3241. JFTOT data shown below in Table IV were developed using a thermally stable fuel, Fuel No. 1, having a break point greater than 371 C (700 F) and a less stable fuel, Fuel No. 2, having a break point at 284 C (541 F). Test data for these fuels were developed at 371 C (700 F) and 271 C (520 F), respectively.

TABLE IV
THERMAL OXIDATION STABILITY TEST, ASTM-D-3241

Jet Fuel	DCI-6A Lb/1000 bbl	Max. Visual Rating*	Max. Pressure Drop, mm Hg**
Fuel No. 1	None	1	0
	8	1	0
Fuel No. 2	None	1	0
	8	2	0

* Passing rating is 3 or less
**Passing rating is 25 mm Hg or less.

COMPATIBILITY WITH OTHER APPROVED CORROSION INHIBITORS

DCI-6A is compatible with all corrosion inhibitors on the Qualified Products List (QPL) of specification MIL-I-25017C. No visual evidence of precipitation or cloudiness occurred when JP-4 fuel containing 8 lb DCI-6A/1000 bbl was mixed with an equal volume of JP-4 containing the other approved inhibitors at their maximum allowable concentrations.

COMPATIBILITY WITH OTHER ADDITIVES

DCI-6A is compatible with other commonly used fuel additives including anti-oxidants, metal deactivators, metal suppressors, gasoline multifunctional additives, fuel oil additives, and anti-icers.

HANDLING PROPERTIES

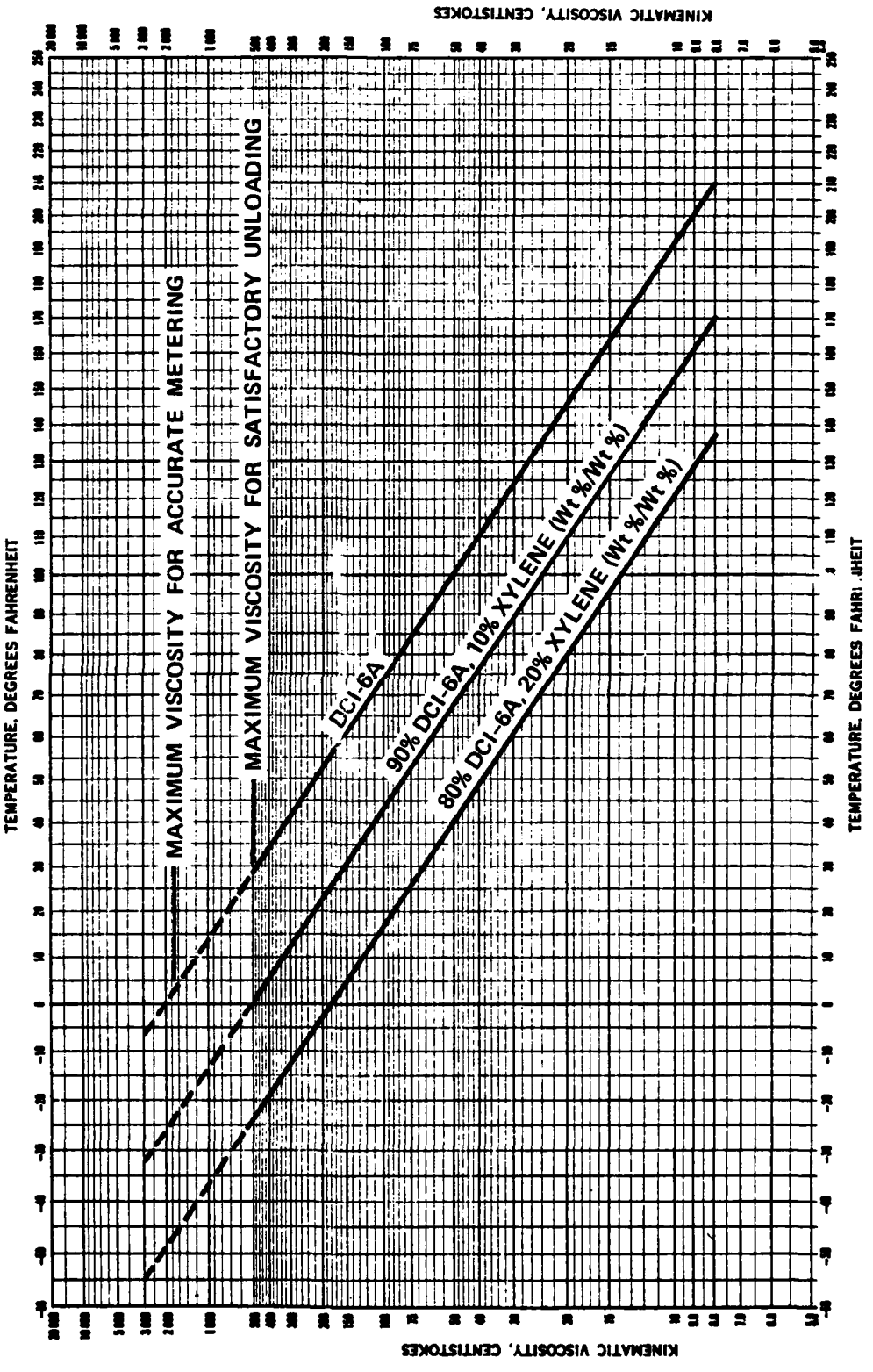
DCI-6A has good low temperature handling properties. Xylene may be added to facilitate unloading characteristics at temperatures below 30 F (-1 C) if desired. The viscosity versus temperature characteristics of DCI-6A are shown in Figure I. Viscosity curves for xylene dilutions of DCI-6A are also shown.

DCI-6A has been stored at 140 F (60 C) for periods in excess of six months without deleterious effect on product quality.

DCI-6A may be added to a fuel either concentrated or in a stock solution using a pump or an eductor system.

Figure 1

VISCOSITY CHARACTERISTICS OF DCI-6A



PRECAUTIONS IN HANDLING

Flammable. Causes Irritation. Keep away from heat, sparks and open flame. Keep container closed. Use with adequate ventilation. Avoid contact with eyes, skin and clothing. Wash thoroughly after handling.

In case of fire, use water spray, foam, dry chemicals or CO_2.

FIRST AID

In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician. Wash skin with soap and plenty of water.

PACKAGES AND SHIPPING POINTS

The standard package for DCI-6A is a non-returnable 55-gallon steel drum containing 400 lb net and having a tare weight of 50 lb. Drum shipments are made from Deepwater, New Jersey, and the following warehouses:

Billings, Montana	Kansas City, Missouri
Chicago, Illinois	Los Angeles, California
Houston, Texas	

Amounts smaller than the standard package are available upon request. Bulk shipments are available by tank car or tank truck from Deepwater, New Jersey.

ADDITIONAL INFORMATION

Additional information and samples can be obtained from any of the Du Pont Petroleum Chemicals Division offices listed on page 8.

DU PONT
Petroleum Chemicals

FOA-3

FUEL OIL ADDITIVE No. 3

FOA-3 is an outstanding antioxidant for diesel and fuel oils. It is ashless, has excellent handling properties, is not extracted by water, and does not contribute to water hazing or emulsification. Maximum benefits can be obtained by the addition of FOA-3 to fresh fuel oil, or to its components, as it comes from the production unit or as soon thereafter as is practical. FOA-3 is compatible with other fuel additives and may be used to advantage in combination with such products as Du Pont Metal Deactivator and dispersant-type additives such as Du Pont FOA-2.

USE CONCENTRATIONS

Recommended use concentrations for FOA-3 will vary with the fuel. It is expected that dosage will range from 1 to 20 lb/1000 bbl (approx. 4 to 70 ppm).

PHYSICAL PROPERTIES

Du Pont Fuel Oil Additive No. 3 is a straw colored liquid having an amine odor and is characterized by the following typical properties:

Ash, wt %		0.00	
ASTM Color		L1.0	
Density, g/ml at 60 F (16 C)		0.86	
Density, lb/gal at 60 F (16 C)		7.2	
Flash Point, Tag Closed Cup		104 F (40 C)	
Pour Point		Below - 70 F (-57 C)	
Base Number (TBN-E), mg KOH/g		425	
Solubility in Kerosine		Completely soluble	
Solubility in No. 2 Fuel Oil		Completely soluble	
Solubility in Water		Approx. 1.5%	
Viscosity,	Temperature	cSt	SUS
	210 F (99 C)	0.6	-
	100 F (38 C)	1.2	-
	0 F (-18 C)	3.3	37

STABILIZATION

FOA-3 retards the formation of color and other degradation products in fuel oils. In laboratory accelerated storage stability tests, FOA-3-treated fuels show significantly less insoluble residue formation and better color than untreated fuels. The data accumulated in such tests and brief descriptions of the test procedures are presented in the following sections.

Advantage of Early Addition of FOA-3

FOA-3 is particularly effective when added to hot, freshly produced fuels and provides the lowest treating cost, for a given stability level, of all the commercially available fuel oil antioxidants. Antioxidants probably function by interfering with reactions involving sulfur, nitrogen, and oxygen containing compounds in the fuel which, if unchecked, form products which are both insoluble in the fuel and cause color formation. Because of the manner in which amines function, it is generally desirable to add them to the unstable, cracked components of the fuel as early as possible in the refining process.

Du Pont Technical Memorandum FO-5019, "Advantages of Early Addition on the Performance of Du Pont FOA-3 and Other Amines as Fuel Oil Stabilizers" discusses this feature in more detail.

ASTM D 2274-70 Accelerated Stability Test for Distillate Fuel Oil

This procedure involves aging fuel at 203 F (95 C) for 16 hours while oxygen is bubbled through the sample. Reductions in insolubles and color stabilization were obtained by the use of FOA-3 in this test as shown below:

FOA-3 IMPROVES THE STABILITY OF NO. 2 FUEL OIL IN THE ASTM D 2274 TEST

FOA-3 Conc., lb/1000 bbl	Total Insolubles, mg/100 ml, Fuel Oil						Filtrate Color - ASTM D 1500 (Initial Color in Parenthesis), Fuel Oil					
	A	B	C	D	E	F	A (1.5)	B (4.0)	C (1.0)	D (L2.0)	E (L1.5)	F (L1.0)
None	5.7	1.3	4.9	2.3	6.9	3.0	5.0	5.0	4.0	3.5	L5.5	L3.5
5	0.7	0.8	1.1	0.9	0.8	1.2	2.5	5.0	3.0	L3.5	L2.5	L2.5
10	0.6	0.8	0.9	0.8	0.7	1.0	2.5	L5.0	L3.0	L3.5	2.0	2.0
15	0.6	0.7	0.7	0.7	0.5	0.7	2.5	L5.0	L3.0	L3.5	L2.0	L2.0

NOTE: 1 lb/1000 bbl equals 2.85 ppm on a weight/volume basis. For distillate fuels of 0.84 specific gravity, 1 lb/1000 bbl equals approximately 3.4 ppm on a weight/weight basis.

300 F Accelerated Test – Du Pont Petroleum Laboratory Method F 21-61

In this procedure, samples are aged for 90 minutes at 300 F (149 C), allowed to cool, and filtered through paper. Performance of the fuels is expressed in terms of a visual rating scale of 1 to 20 based on the amount of material on the filters. The lower the rating the more stable the fuel. Many fuels exhibit excellent response to FOA-3 in this test as shown in the following table.

FOA-3 IMPROVES HIGH TEMPERATURE STABILITY IN THE 300 F (149 C) TEST

FOA-3 Conc., lb/1000 bbl	Filter Rating (1 = Clean) Fuel Oil								
	A	B	C	D	E	F	G	H	I
None	19	12	17	13	20	15	18	12	18
5	7	8	12	7	7	9	3	-	11
7.5	-	-	-	-	-	-	-	1	-
10	5	8	5	5	4	9	-	-	-
15	5	7	4	4	3	9	-	-	-
	Filtrate Color - ASTM D 1500 (Initial Color in Parentheses)								
	(1.5)	(4.0)	(1.0)	(L2.0)	(L1.5)	(L1.0)	-	-	-
None	D8.0	6.5	7.5	L5.0	D8.0	5.5	D8.0	L3.0	D8.0
5	4.0	5.5	5.5	L3.5	L4.0	L4.5	L2.5	-	L2.5
7.5	-	-	-	-	-	-	-	L1.5	-
10	3.0	5.5	4.0	3.0	L3.0	L4.5	-	-	-
15	3.0	5.5	3.5	L3.0	L2.5	L4.0	-	-	-

110 F Storage Test

In this test, fuel is stored at 110 F (43 C) in vented bottles and periodic determinations are made of changes in significant properties. One week in 110 F (43 C) storage is considered approximately equivalent to one month in normal field storage.

As shown by the data in the following table, FOA-3 provides good control of insoluble residue in this test.

EFFECT OF FOA-3 ON STORAGE STABILITY
IN 110 F (43 C) STORAGE TESTS

FOA-3 Conc., lb/1000 bbl	Weeks at 110 F (43 C)	Insoluble Residue, mg/100 ml Fuel Oil			Filtrate Color - ASTM D 1500 (Initial results in parenthesis) Fuel Oil		
		A	B	C	A	B	C
None	0	0.6	0.4	0.3	(1.5)	(4.0)	(1.0)
	4	2.4	1.4	1.2	3.5	5.0	3.5
	8	4.6	2.2	3.1	L5.5	L5.5	4.0
10	4	1.1	0.6	0.8	2.5	5.5	3.5
	8	0.7	1.6	1.4	2.5	L5.5	L4.5
20	4	0.9	1.3	0.9	2.5	5.5	3.5
	8	0.8	1.9	1.3	2.5	L5.5	4.5

Great Lakes Pipeline Accelerated Stability Test for No. 2 Fuel Oils

In this test, samples of fuel oil are aged 16 hours at 212 F (100 C) under 100 psig oxygen in a bomb, then cooled, filtered and the soluble, insoluble and total gum determined. The color of the filtrate is also measured.

FOA-3, alone or in combination with DMD, is effective in reducing gum formation in this test as is evidenced by the data summarized in the table on the opposite page.

WATER EXTRACTABILITY

Samples of fuel with and without FOA-3 were shaken vigorously for 10 minutes with ten percent tap water. The 300 F stability test (Petroleum Laboratory Method F21-61) was run on the samples both before and after water extraction. Water washing had no effect on the stabilization properties of FOA-3 as illustrated in the following table:

STABILIZATION OF FUEL CONTAINING FOA-3 IS NOT
AFFECTED BY WATER WASHING

(300 F Accelerated Stability Test)

FOA-3, lb/1000 bbl	Blotter Rating		Color - ASTM D 1500	
	Unwashed	Washed	Unwashed	Washed
0	17	16	L8.0	7.0
7.5	1	1	L1.5	L1.5

FOA-3 RETARDS GUM FORMATION
IN THE GREAT LAKES PIPELINE TEST

Additive Concentration, lb/1000 bbl	Gum, mg/100 ml			Color, ASTM D 1500
	Soluble	Insoluble	Total	
Fuel G				
None	31.2	17.2	48.4	L6.0
6 FOA-3	12.6	4.2	16.8	L4.0
5 FOA-3 + 0.5 DMD	9.6	2.2	11.8	L3.5
Fuel H				
None	26.4	14.4	40.8	5.5
5 FOA-3	12.4	5.6	18.0	L4.0
35 FOA-3	4.8	3.8	8.6	3.0
Fuel I				
None	51.6	27.2	78.8	L7.0
3 FOA-3	33.6	16.2	49.8	L6.5
5 FOA-3	24.4	13.6	38.0	L6.5
7.5 FOA-3	23.2	12.4	35.6	L5.5
10 FOA-3	19.4	7.6	27.0	L5.0
15 FOA-3	14.8	4.4	19.2	L4.5
3 FOA-3 + 0.5 DMD	30.8	13.6	44.4	L6.0
5 FOA-3 + 0.5 DMD	24.0	11.6	35.6	L5.5
15 FOA-3 + 0.5 DMD	9.4	3.4	12.8	L3.5

WATER CONTACT PROPERTIES

Because of its chemical composition, FOA-3 has little or no effect on the tendency of fuel oils to form haze or emulsions when mixed with water. Also, FOA-3 has no adverse effect on the rate of water settling.

The photographs on pages 6 and 7 show the effects on water settling rate when FOA-3 was added to fresh, wet refinery fuels. Results of laboratory tests which measure emulsion-forming tendencies and water settling rate are presented on page 8.

EFFECT OF FOA-3 ON WATER SETTLING RATE

FOA-3 was added to fresh, wet fuel from catalytic crackers at two Mid-Western refineries and the water settling rate compared to that of nonadditive fuel. FOA-3 had no adverse effect on water settling as is demonstrated in the following pictures.

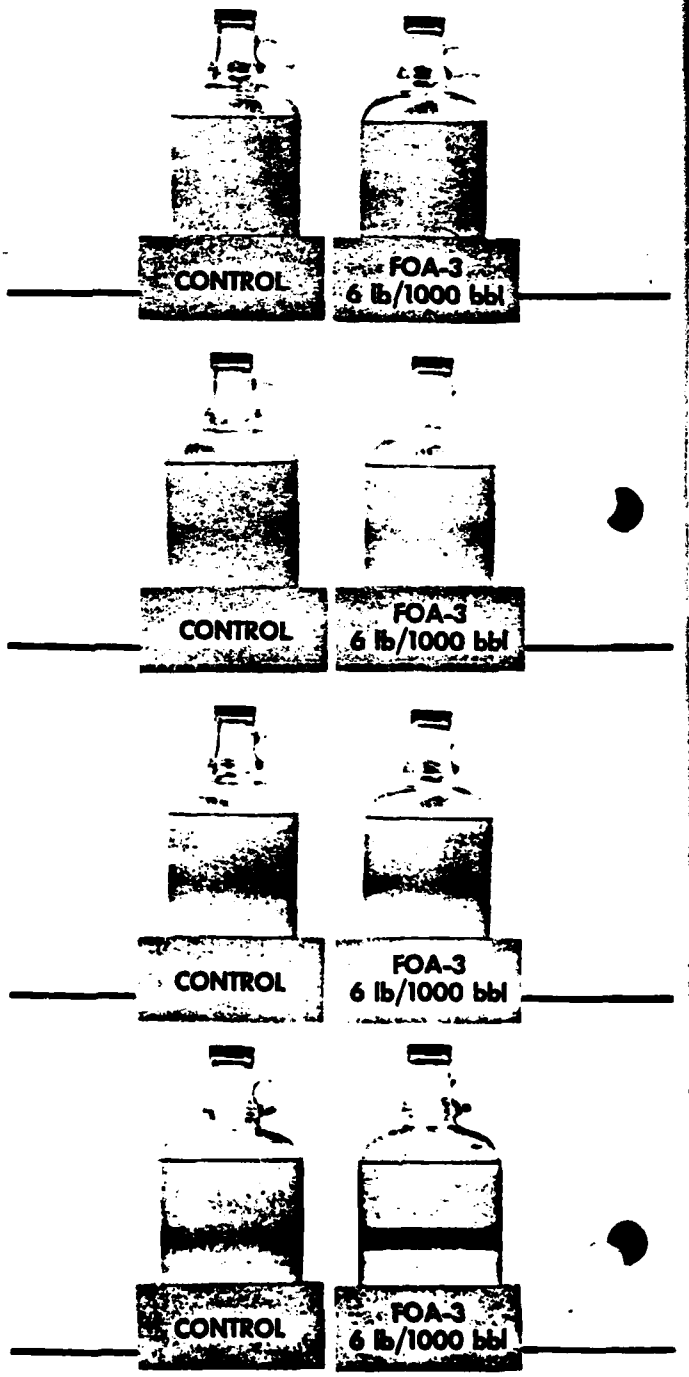
FUEL L

FRESH FUEL

SETTLED 1 DAY

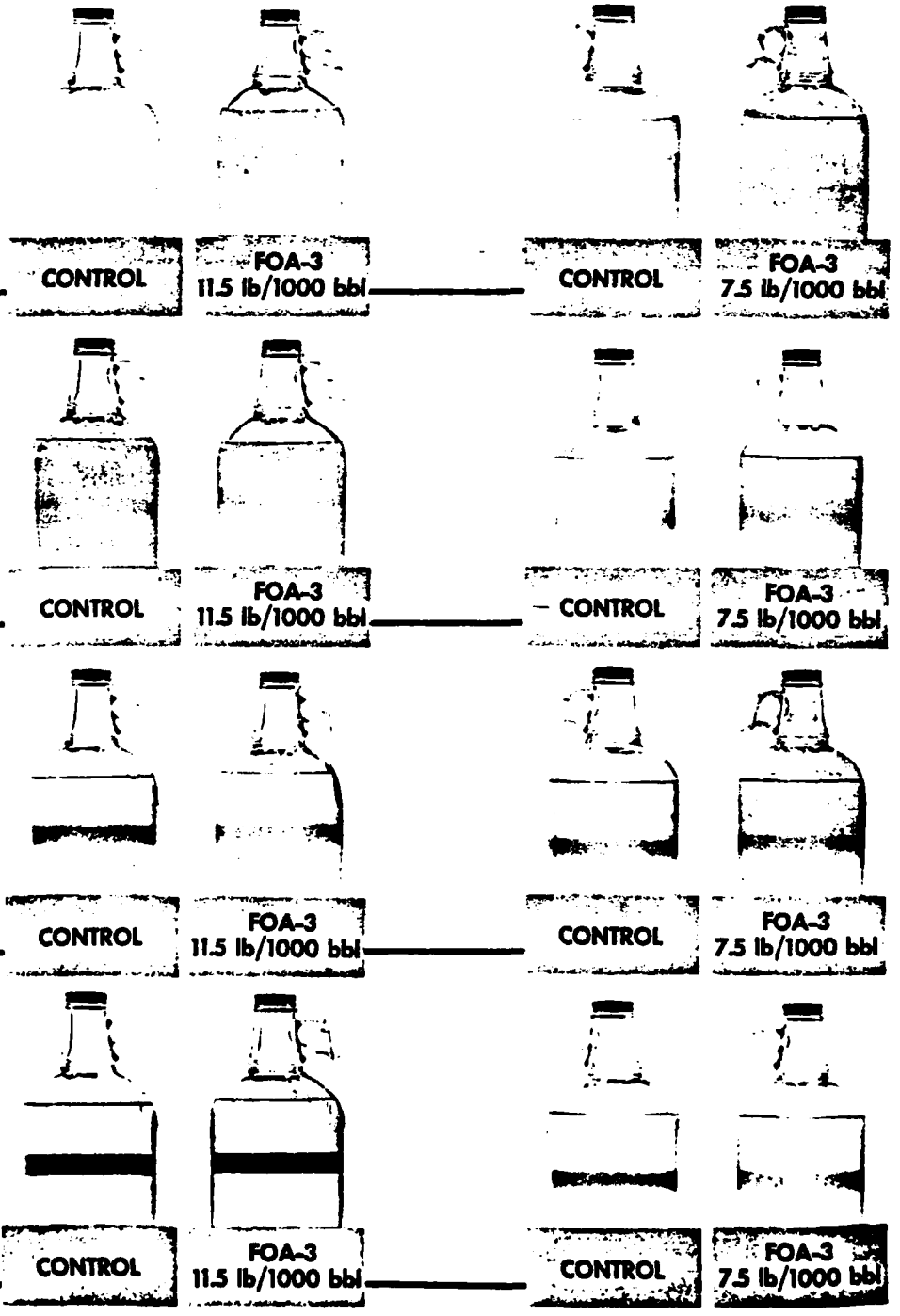
SETTLED 2 DAYS

SETTLED 3 DAYS



FUEL M

FUEL N


CONTROL
FOA-3
11.5 lb/1000 bbl
CONTROL
FOA-3
7.5 lb/1000 bbl
CONTROL
FOA-3
11.5 lb/1000 bbl
CONTROL
FOA-3
7.5 lb/1000 bbl
CONTROL
FOA-3
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FOA-3
7.5 lb/1000 bbl
CONTROL
FOA-3
11.5 lb/1000 bbl
CONTROL
FOA-3
7.5 lb/1000 bbl

ANTIEMULSION AND ANTIHAZE PROPERTIES

Oil Change Emulsion Test

The Oil Change Emulsion Test measures the tendency of distillate oils to form emulsions in the presence of water. In this test, oil is agitated violently with 5% of water for five minutes in a high speed mixer. If, after standing for 24 hours, no emulsion remains, the procedure is repeated using the same water and a fresh oil sample. The number of oil changes that can be made without creating an emulsion is taken as the criterion of performance.

The following table shows FOA-3 has no effect on the emulsification properties of fuel oils:

EFFECT OF FOA-3 ON EMULSION FORMATION IN THE OIL CHANGE TEST

FOA-3 Conc., lb/1000 bbl	Number of Changes Required to Develop Emulsion		
Fuel:	B	J	K
None	3	3	7
20	3	3	7

Haze Test

Fuel containing 0.2% water is agitated in a milkshake mixer for 5 minutes. The amount of haze is measured by withdrawing small samples of fuel periodically for light-transmission measurements with a Lumetron colorimeter.

FOA-3 has little or no effect on water settling rate in this test as shown in the table below:

EFFECT OF FOA-3 ON WATER SETTLING RATE IN HAZE TEST

Fuel	FOA-3 Conc., lb/1000 bbl	Light Transmission, % Hours After Mixing			
		0	2	24	48
B	None	32	78	97	97
B	20	35	84	98	98
K	None	43	54	98	99
K	20	54	61	98	98

PRECAUTIONS IN HANDLING

Causes burns (as defined by DOT skin corrosivity test). Combustible. Harmful if swallowed or inhaled. Do not get in eyes, on skin or clothing. Keep away from heat and open flame. Avoid breathing vapor. Keep container closed. Use with adequate ventilation. Wash thoroughly after handling.

In case of fire, use water spray, foam, dry chemical or CO_2.

FIRST AID

In case of contact, immediately flush eyes with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse.

If inhaled, remove to fresh air. If not breathing, give artificial respiration, preferably, mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

If swallowed, induce vomiting until vomit is clear. Call a physician. Never give anything by mouth to an unconscious person.

PACKAGING AND SHIPPING POINTS

The standard package for FOA-3 is a non-returnable 55 gallon (208 liter) steel drum containing 386 lb (175 kg) net and having a tare weight of 50 lb (22.7 kg). Drum shipments are made from Deepwater, New Jersey, and the following warehouses:

Billings, Montana	Houston, Texas
Berlin, Illinois	Kansas City, Missouri
Des Plaines, Illinois	Los Angeles, California

Amounts smaller than the standard package are available upon request. Bulk shipments are available by tank car or tank truck from Carneys Point, New Jersey.

APPENDIX A
PART 2

Ethyl Corporation

"Ethyl" Antioxidants in Fuels

733, 735, 701, PDA, PDA(D), PDA(H), MDA, and 733 Mixtures

"ETHYL" ANTIOXIDANTS FOR PETROLEUM PRODUCTS

Commercial products available from Ethyl's patented ortho-alkylation process include "Ethyl" Antioxidants 701, 702, 703, 728, 733, and 735.*

This technical brochure describes the use of *733, 735, and 701* in fuel applications including motor and aviation gasolines, jet fuels, and fuel-sweetening processes. Other additives described are three phenylenediamine additives—the widely used di-*sec*-butyl product (PDA) and its diisopropyl and diheptyl analogs (PDA-D and PDA-H) and the conventional metal deactivator (MDA). Included are compositions and application data on mixtures of "Ethyl" 733 with these additives and with toluene.

*Ethyl has a continuing program of antioxidant synthesis and evaluation. Developmental products can be made available on request.

There are two other technical brochures on "Ethyl" antioxidants in lubricants and industrial oils.

ANTIOXIDANTS FOR LUBRICANTS

Describes the properties and uses of "Ethyl" Antioxidants 702, 728, and 703 in lubricant applications such as motor oils, aviation, railroad diesel, marine, 2-cycle, and transmission fluids, and severe-duty industrial oils

INDUSTRIAL OIL ANTIOXIDANTS

Describes the properties and uses of "Ethyl" 733, 735, and 701 in industrial oils. Included are results on these additives in hydraulic, steam turbine, gear, and transformer oils.

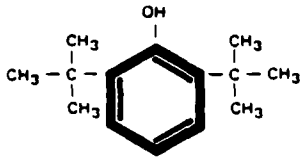
Technical information on two new hydraulic oil additives, HOA-22 and HOA-44, is presented.

Ethyl Corporation has an experienced technical staff ready to assist on applications involving antioxidants or other Ethyl additives.

	702	728	703	701	733	735	HOA-22	HOA-44	PDA	PDA(D)	PDA(H)	MDA	733 Mixtu*
LUBRICANTS	●	●	●										
Motor	●	●	●										
Aviation	●	●	●										
Railroad Diesel	●	●											
Gas Engine	●	●											
Marine	●	●											
Two-Cycle	●	●											
Diesters			●										
Greases			●										
INDUSTRIAL OILS	●	●	●	●	●	●	●	●					
Steam Turbine				●	●	●	●	●					
Transformer				●									
Hydraulic	●	●	●	●	●	●	●	●					
Gear	●	●	●	●	●	●	●	●					
Transmission Fluids	●	●	●	●	●	●	●	●					
FUELS	●	●	●	●	●	●			●	●	●	●	●
Distillate	●	●	●	●	●	●			●	●	●	●	●
Motor				●	●	●			●	●	●	●	●
Aviation				●	●	●			●	●		●	●
Jet				●	●	●			●	●		●	●

733

For Use In: Motor Gasolines, Aviation Gasolines, Jet Fuels, Industrial Oils.



2, 6-di-*tert*-butylphenol

"Ethyl" Antioxidant 733 is a low-cost liquid mixture of hindered phenols. It consists of mixed *tert*-butylphenols with the following typical composition:

2,6-Di-*tert*-butylphenol ("ETHYL" 701) —75% MIN

2,4,6-Tri-*tert*-butylphenol
Ortho-*tert*-butylphenol } —25% MAX

Ortho-*tert*-butylphenol —10% MAX

Physical Properties (Typical)

Form	Liquid
Color	Yellow
Density @ 68°F (20°C)	
g/ml	0.94
lb/U.S. gal.	7.8
Freezing Point, °F (°C)	63 (17)*
Flash Point (COC), °F (°C)	>200 (>93)
(TCC), °F (°C)	38 (3)
Viscosity	
SUS @ 68°F (20°C)	115
cSt @ 40°C (104°F)	6.33
ISO VG (ASTM D 2422)	7
Solubility @ 68 °F (20 °C)	**Wt %**
In Toluene	Miscible
In Water	0.01**
In 10% NaOH	10 max.†
In 1% H_2SO_4	Insoluble

* Tends to supercool.

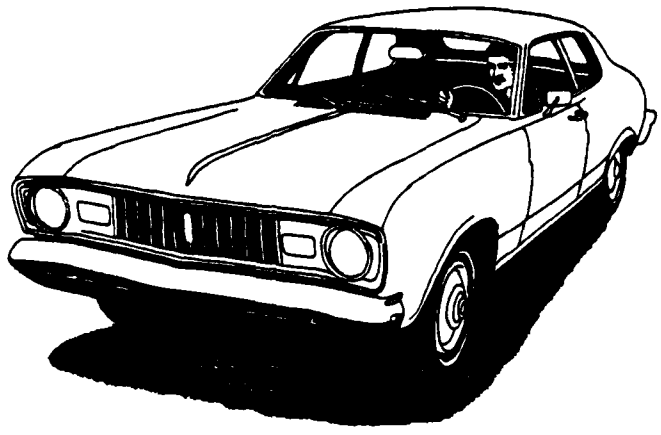
** Only ortho-*tert*-butylphenol is partially soluble.

† The 2, 6 and 2, 4, 6 substituted phenols are insoluble; the ortho-*tert*-butylphenol is soluble.

Uses

In both motor and aviation gasolines, "Ethyl" 733 has proved to be equal or superior to commercial trialkylphenol and phenylenediamine antioxidants in controlling both formation of gum and peroxides and decomposition of anti-knock compounds. Unlike some other fuel antioxidants, it does not contribute to induction system deposits.

"Ethyl" 733 effectively inhibits the formation of soluble and insoluble decomposition products of jet fuels during storage. It is also an effective antioxidant for steam-turbine oils and other industrial oils.



Structural Effectiveness

In recent years, a number of lower-cost antioxidants made from phenolic mixtures obtained from coal tar byproducts or refinery streams have been introduced. Judging from the limited compositional information provided by the suppliers, the hindered phenol content of these additives ranges from zero to 60%.

It has been well established in the chemical literature that antioxidant effectiveness requires steric hindrance to the hydroxyl group brought about by the presence of alkyl substituents in both ortho (2 and 6) positions.* At least one of these substituents, and preferably both in the case of turbine oil antioxidants, should be tertiary butyl groups.† For "Ethyl" 733, 90% is completely hindered phenols (tertiary butyl groups in both 2 and 6 positions), with the remaining 10% having one tertiary butyl group in the ortho position.

MOTOR GASOLINES

Antioxidants of low or moderate effectiveness may perform well in very stable fuels in quick tests, such as the induction period test. However, long-term storage tests at 110 °F (43 °C) are the true measure of stability in terms of protection against fuel or antiknock deterioration.**

* Gilks, J. H., "Antioxidants for Petroleum Products," *Inst. Petroleum, 50,* 309 (1964).

† Wasson, J. I. and Smith, W. M., "Effect of Alkyl Substitution on Antioxidant Properties of Phenols," *Ind. Eng. Chem., 45,* 197 (1953).

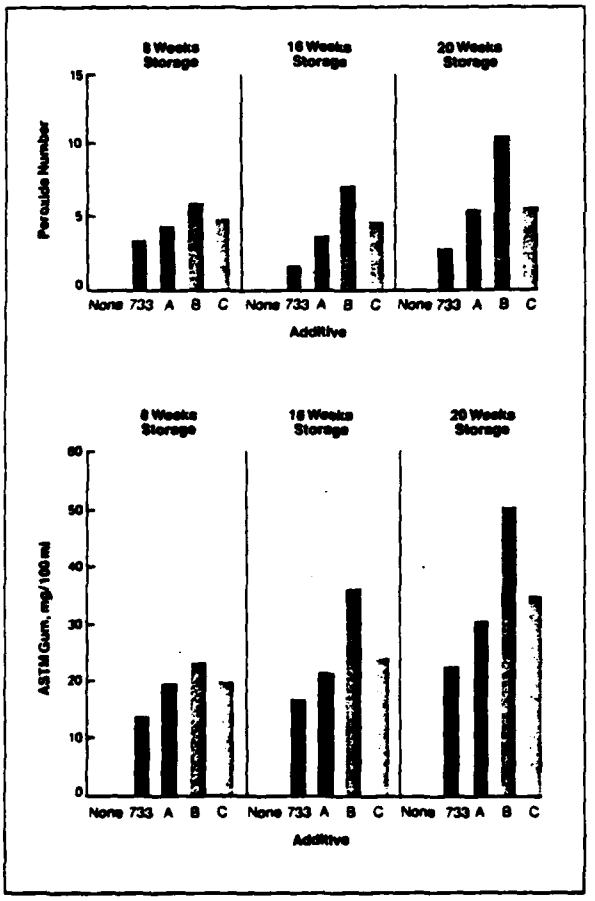
** Bartleson, J. D. and Shepherd, C. C., "How to Select Gasoline Antioxidants," *Hydrocarbon Processing, 43,* 153, August 1964.

Storage Tests/1

A 110°F (43°C) storage test comparison was made at a concentration of 2 lb./1000 bbl in a major brand regular-grade gasoline containing 2.5g Pb/U.S. gallon as TEL between "Ethyl" 733 and three commercial mixed phenolic additives having the following stated compositions:

Additive	Composition
"Ethyl" 733	75% 2, 6-di-*tert*-butylphenol + 25% 2, 4, 6-tri-*tert*-butylphenol and ortho-*tert*-butylphenol
A	DBPC and other alkylated phenols
B	40% 2, 4, 6-trimethylphenol and other methylphenols
C	60% 2, 4-di-*tert*-butylphenol + 40% mixed *tert*-butylphenols

The results show that "Ethyl" 733 was better than the other three additives on both ASTM gum and peroxide number in every comparison measurement at each of the three sampling periods of 8, 16, and 20 weeks. The poorest of the additives evaluated (Additive B), which was only slightly better than the base fuel, had a zero content of hindered phenol.



Storage Tests/2

In another 110°F (43°C) storage test, "Ethyl" 733 at a concentration of 1 lb/1000 bbl was compared with Additive C at concentrations of 1, 2 and 3 lb/1000 bbl for 11 weeks. The base fuel was a regular-grade commercial gasoline containing 3g Pb/U.S. gallon as MLA-500.

Additive @ lb/1000 bbl	ASTM Gum, mg/100 ml			Soluble Alkyl Lead Salts, mg Pb/100 ml		
	4 wks	7 wks	11 wks	4 wks	7 wks	11 wks
733 (1 lb)	3.4	5.4	7.4	0.93	1.09	1.40
C (1 lb)	8.4	7.8	11.0	1.10	1.29	1.44
C (2 lb)	8.4	8.0	11.2	1.16	1.44	1.59
C (3 lb)	8.0	7.8	11.2	1.18	1.44	1.61

Additive C failed to provide protection against gum formation (allowable gum is 7 mg) for even 4 weeks of storage at any concentration, while "Ethyl" 733 at 1 lb/1000 bbl was effective for 7 weeks.

Similarly, "Ethyl" 733 at 1 lb/1000 bbl gave better stabilization against lead decomposition than Additive C, which again showed no improvement as concentration was increased.

"Ethyl" 733 has been used successfully in industrial oils for many years (see brochure on "Ethyl" Antioxidants 701, 733, and 735 for Industrial Oils). This is a more severe application than motor gasolines because of the higher te[illegible] encountered in service and laboratory studies. The mixed phenolic additives described above are not recommended for industrial oils, presumably because of their low content of hindered phenol active ingredient.

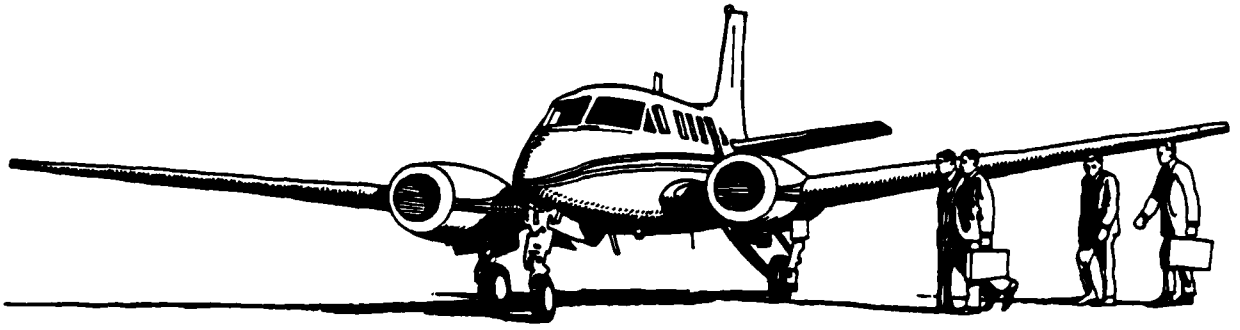
"Ethyl" 733 has been found to be equal or superior to a commercial trialkylphenol (DBPC) and phenylenediamine (PDA) antioxidants in controlling formation of gum, peroxides (Peroxide No.), and soluble alkyl lead salts (SALS), based on storage tests at 110°F (43°C). For example, the following tables compare storage performance in two different fuels containing 3 ml TEL (3.17g Pb)/U.S. gallon.

FUEL A (Full-boiling-range catalytically cracked gasoline)

Storage Time in Weeks	Antioxidant (7 lb/1000 bbl)					
	0	8	16	24	32	36
733 Gum (mg/100 ml)	4	4	4	6	6	7
Peroxide No.	0.5	—	—	0.7	—	1.0
DBPC Gum(mg/100 ml)	4	4	4	7	7	11
Peroxide No.	0.5	—	—	1.4	—	6.0

FUEL B (Finished blend of catalytically cracked, straightrun and polymer gasolines)

Storage Time in Weeks	Antioxidant (2 lb/1000 bbl)		
	0	8	20
733 Gum (mg/100 ml)	2	1	2
SALS	0.1	0.3	0.4
PDA Gum (mg/100 ml)	2	1	1
SALS	0.1	0.3	0.5



AVIATION GASOLINES

"Ethyl" 733 gives excellent protection against TEL decomposition, based on storage tests at 110°F (43°C). Formation of soluble alkyl lead salts (SALS) and precipitate (PPT) are measures of this decomposition tendency. For example, in Fuel C containing 4.86g Pb/U.S. gallon as TEL.

FUEL C (Aviation Alkylate)

Storage Time in Weeks		Antioxidant (4 lb/1000 bbl)						
		0	3	6	12	18	24	30
None	SALS	0.8	6.1	16.5	(Test discontinued)			
	PPT	None	Med.	V.H.	(Test discontinued)			
733	SALS	0.6	0.6	0.6	0.6	0.7	0.8	0.8
	PPT	None	None	None	None	None	None	None
DBPC*	SALS	0.6	0.6	0.9	0.9	0.9	0.9	1.2
	PPT	None	None	None	None	None	None	Slight
PDA	SALS	0.6	0.6	0.7	0.7	0.7	0.9	1.7
	PPT	None	None	None	None	None	None	None

*Trialkyl phenol

JET FUELS

There has been renewed interest in jet fuel antioxidants because of a recent amendment to Military Specification MIL-T-5624K (JP-4, JP-5), which also includes MIL-T-83133 (Turbine Fuel, Aviation, Kerosene Type, Grade JP-8.) The new paragraph 3.3.1, titled "Antioxidants," in Amendment 1 to MIL-T-5624K dated November 12, 1976, reads as follows:

"3.3.1 *Antioxidants.* Immediately after processing add an approved antioxidant in order to prevent the formation of gums and peroxides after manufacture. The concentration of antioxidant to be added shall be:

"a. Not less than 6.0 lbs. nor more than 8.4 lbs. of active ingredient per 1,000 barrels of fuel (17.2 to 24.0 mg/l) to all JP-5 fuels and to JP-4 fuels that contain blending stocks that have been 'hydrogen treated.'

"b. At the option of the supplier, not more than 8.4 lbs. of active ingredient per 1,000 barrels of fuel (24.0 mg/l) may be added to JP-4 fuels that do not contain any 'hydrogen treated' blending stocks."

Three "Ethyl" Antioxidants (701, 733, and 735), all based on 2, 6-di-*tert*-butylphenol, are approved in MIL-T-5624K and are now being used. One of the most difficult specification tests for JP-4 and JP-5 jet fuels is the "Water Separation Index" (ASTM D-2550); at least one of the three approved Ethyl antioxidants usually will provide a passing result in this test.

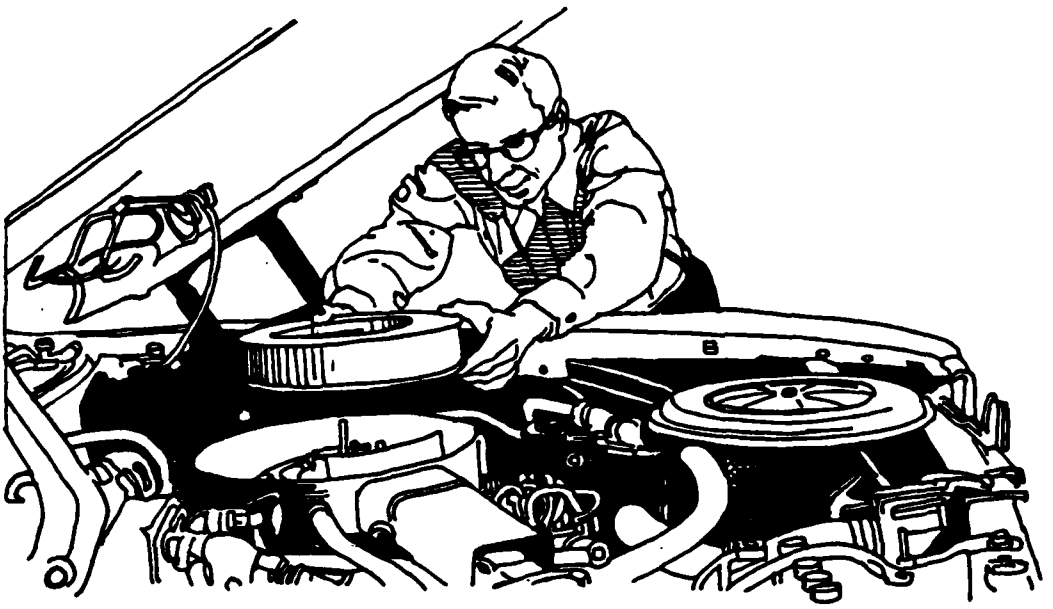
"Ethyl" Antioxidants 701, 733, and 735 are described in MIL-T-5624K in the following manner in paragraph 3.3.1.

"3.3.1-e 2, 6-di-*tert*-butylphenol ("Ethyl" Antioxidant 701)
"3.3.1-f 75 percent min. 2, 6-di-*tert*-butylphenol
25 percent max. *tert*-butylphenols and tri-*tert*-butylphenols ("Ethyl" Antioxidants 733 and 735.)"

Typical compositions, physical properties, and solubilities of the three approved "Ethyl" jet fuel antioxidants are shown in the following tables.

Typical Compositions

Compound	Percent		
	701	733	735
ortho-*tert*-butylphenol	0.4	7.4	Nil
2, 6-di-*tert*-butylphenol	98.1	75.7	85
2, 4, 6-tri-*tert*-butylphenol	0.4	12.2	11
2, 4-di-*tert*-butylphenol + other phenols	1.1	4.7	4



Physical Properties (Typical)

	701	733	735
Form	Solid	Liquid	Partially Solid
Color	Light Straw	Yellow	Y 'low
Molecular Weight	206.3		
Boiling Point, °F (°C) @ 760 mm Hg	487 (253)	436-507 (224-264)	481-507 (249-264)
Flash Point (COC), °F (°C)	>200 (>93)	200 (93)	260 (127)
(TCC), °F (°C)	>210 (>99)	38 (3)	>210 (>99)
Melting Point, °F (°C)	97 (36)	-	80 (27)*
Freezing Point, °F (°C)	-	63 (17)*	-
Density @ 68°F (20°C) g/ml	0.914	0.94	-
lb/U.S. gal.	7.61	7.8	-
@ 80°F (27°C) g/ml	-	-	0.95
lb/U.S. gal.	-	-	7.9
Density Temperature Correction Factor 85-140°F, g/ml per °F	-	0.000400	0.000427
29-60°C, g/ml per °C	-	0.000722	0.000769
Viscosity SUS @ 68°F (20°C)		115	
SUS @ 100°F (38°C)	49.9		55.0
SUS @ 210°F (99°C)			32.0
cSt @40°C (104°F)	6.64	6.33	8.05
ISO VG (ASTM D 2422)	7	7	7

*Tends to supercool.

The major difference in physical properties due to composition is the freezing point of 63°F (17°C) for 733 and the melting points of 80°F (27°C) for 735 and 97°F (36°C) for 701.

Solubility

Solubility @ 68°F (20°C)	Wt %		
	701	733	735
In Water	Insoluble	0.01*	Insoluble
In 10% NaOH	Insoluble	10 max.†	Insoluble
In Toluene	Soluble	Miscible	Soluble
In 1% H_2SO_4	Insoluble	Insoluble	Insoluble
In Motor Oil	Soluble	Soluble	Soluble
In Gasoline	Soluble	Soluble	Soluble

*Only ortho-*tert*-butylphenol is partially soluble.

†The 2, 6 and 2, 4, 6 substituted phenols are insoluble; the ortho-*tert*-butylphenol is soluble.

"Ethyl" Antioxidants 701, 733, or 735 diluted with toluene or other aromatic solvents can be supplied if lower freezing points are required. Examples of 733-toluene mixtures and their freezing points are shown on Page 11.

Another change in Military Specification MIL-T-5624K, effective May 20, 1977 removed

- N, N'-Diisopropyl-*p*-phenylenediamine
- N, N'-Di-*sec*-butyl-*p*-phenylenediamine
- 65 percent N, N'-Di-*sec*-butyl-*p*-phenylenediamine
  35 percent N, N'-Di-*sec*-butyl-*o*-phenylenediamine

from the list of acceptable additives.

Two reasons were stated for removing these products.

1. These antioxidants "form color bodies in the fuel ranging from pink to tan. When these fuels are tested with the AEL MK111 contaminated fuel detector, the color bodies are adsorbed on the filters, resulting in high readings indicative of fuel containing solid contaminants."
2. "Research with these amine-type antioxidant additives has also indicated that this chemical class of antioxidant interferes with other additives occasionally used in the fuel."

PDA

For Use In: Motor Gasolines, Aviation Gasolines, Jet Fuels.

N,N'-Di-*sec*-butyl-*p*-phenylenediamine
(98% minimum purity)

"Ethyl" Antioxidant PDA is the conventional phenylenediamine-type gasoline additive. The product contains no diluent and is essentially 100% active ingredient. In motor gasolines, aviation gasolines, and jet fuels, this product is an excellent oxidation inhibitor and an efficient sweetening catalyst.

Physical Properties (Typical)

Form	Liquid
Color	Brown to Red
Density @ 68°F (20°C)	
g/ml	0.94
lb/U.S. gal.	7.8
Freezing Point, °F (°C)	58 (14)
Flash Point (COC), °F (°C)	>300 (>149)
(TCC), °F (°C)	>295 (>146)
Viscosity	
SUS @ 68°F (20°C)	140
cSt @ 40°C (104°F)	11.32
ISO VG (ASTM D 2422)	10
Solubility @ 68°F (20°C)	**Wt %**
In Toluene	Miscible
In Water	<1
In 10% NaOH	>1
In 1% H_2SO_4	>8

PDA(D)

For Use In: Motor Gasolines, Aviation Gasolines, Jet Fuels.

N, N'-Diisopropyl-*p*-phenylenediamine

"Ethyl" Antioxidant PDA(D) is a diisopropyl structural modification of "Ethyl" Antioxidant PDA. The product is a 50% solution of active ingredient in a mixture of methanol and isopropanol.

In motor gasolines, aviation gasolines, and jet fuels, this product is an excellent oxidation inhibitor and an efficient sweetening catalyst. Relative to "Ethyl" PDA, the diisopropyl product is a more effective sweetening agent and a less effective antioxidant. The primary use of "Ethyl" PDA(D) is in refinery streams where inhibitor sweetening is practiced.

Physical Properties (Typical)

Concentration	50% Active
Form	Liquid
Color	Red
Density @ 60°F (20°C)	
g/ml	0.88
lb/U.S. gal.	7.3
Freezing Point, °F (°C)	28 (-2) (Supercools)
Flash Point (TOC), °F (°C)	70 (21)
(TCC), °F (°C)	60 (16)
Viscosity	
SUS @ 68°F (20°C)	45
cSt @ 40°C (104°F)	3.56
ISO VG (ASTM D 2422)	3
Solubility @ 68°F (20°C)	**Wt %**
In Toluene	Miscible
In Water (active ingredient)	<1
In 10% NaOH (active ingredient)	<1
In 1% H_2SO_4 (active ingredient)	>8

PDA(H)

For Use In: Motor Gasolines

N, N'-bis-(1, 4-dimethylpentyl)-*p*-phenylenediamine

"Ethyl" Antioxidant PDA(H) is a diheptyl structural modification of "Ethyl" Antioxidant PDA. The product contains no diluent and is essentially 100% active ingredient.

In motor gasolines, this product is an excellent oxidation inhibitor and an efficient sweetening catalyst. Relative to "Ethyl" PDA, PDA(H) is equivalent as a sweetener but slightly less effective as an antioxidant.

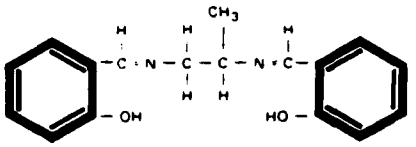
PDA(H) has a significantly lower freezing point than PDA or PDA(D), providing a 100% active ingredient product with excellent low-temperature handling properties.

Physical Properties (Typical)

Form	Liquid
Color	Amber to Red
Density @ 68°F (20°C)	
g/ml	0.90
lb/U.S. gal.	7.5
Freezing Point, °F (°C)	-45 (-43)
Flash Point (COC), °F (°C)	380 (193)
(TCC), °F (°C)	>200 (>93)
Viscosity	
SUS @ 100°F (38°C)	172
cSt @ 40°C (104°F)	27.48
ISO VG (ASTM D 2422)	32
Solubility @ 68°F (20° C)	**Wt %**
In Toluene	Miscible
In Water	<1
In 10% Na OH	<1
In 1% H_2SO_4	>2

MDA

For Use In: Motor Gasolines, Aviation Gasolines, Jet Fuels, Distillate Fuels.



N,N'-disalicylidene-1,2-diaminopropane
(N,N'-disalicylidene propylenediamine)

Ethyl MDA metal deactivators are solutions of N, N'—disalicylidene propylenediamine in xylene. These effective products are offered in two convenient concentrations—Ethyl MDA-80 (80% active ingredient) and Ethyl MDA-50 (50% active ingredient). Ethyl MDA-50 is recommended for cold-weather use.

Physical Properties (Typical)

	MDA-80	MDA-50
Form	Liquid	
Color	Amber	
Density @ 68°F (20°C)		
g/ml	1.07	0.98
lb/U.S. gal.	8.9	8.2
Active Ingredient, wt %	80	50
Solvent (xylene), wt %	20	50
Flash Point (TOC), °F (°C)	85 (29)	91 (33)
(TCC), °F (°C)	97 (36)	72 (22)
Pour Point, °F (°C)	−15 (−26)	−90 (−68)
Viscosity		
SUS @ 100°F (38°C)	109	33.1
cSt @ 40°C (104°F)	9.87	17.76
ISO VG (ASTM D 2422)	10	15
Solubility @ 68°F (20°C)	Wt %	
In Gasoline (Typical)	Saturated solution contains 94% MDA	
In Water	0.04	
Phase Separation Temperature, °F (°C)	85 (29)*	45 (7)*

* Supercools to well below 32° F. After crystallization, mixture must be warmed to 85° F before complete solution occurs.

Uses

Since metal deactivators are usually used in conjunction with an antioxidant, this product is included in this brochure for completeness. "Ethyl" MDA is a fuel additive that neutralizes the catalytic effect of copper in promoting fuel oxidation. No matter how carefully a fuel is refined, its potential storage life can be seriously curtailed by subsequent contact with copper. This contact is almost unavoidable and may come from two major sources: (1) Contamination from transfer or handling systems that employ pumps, valves, or lines made of copper or cuprous-metal alloys; (2) Trace amounts (generally less than 1 ppm) retained in the fuel after a copper sweetening process.

In gasolines, "Ethyl" MDA will lengthen storage life, reduce gum formation, and combat decomposition of antiknock compounds. In higher-boiling distillates, it will help stabilize color and minimize the formation of the gel-like copper mercaptides that are often responsible for filter and nozzle plugging.

Relatively simple tests can determine the amount of copper present in a fuel fresh from the refinery. However, it is essentially impossible to estimate the potential copper contamination that may occur in subsequent fuel-handling operations. Experience has shown that it is economical insurance to arbitrarily provide a sufficient concentration of "Ethyl" MDA to counteract the maximum anticipated copper contamination.

Recommended Concentrations

Calculations for determining "Ethyl" MDA concentrations are based on the use of 0.4 lb MDA/1000 bbl for each 1.0 mg Cu/U.S. gal. (These figures, and subsequent ones, consider only the active ingredient, which is 80 wt % in xylene.)

General Recommendations

A number of refiners have found 1 to 3 lb/1000 bbl desirable for fuels in normal use. This amount is generally sufficient to provide protection throughout the system.

Abnormal Applications

There are circumstances—such as in factory-fill fuels, certain marine installations, etc.—where the fuel may be subjected to excessive exposure to copper. In most such cases, purchase specifications require unusually high concentration of metal deactivator—ranging up to 10 to 15 lb/1000 bbl.

Tests for Copper Content

Copper content can be determined quite accurately by available analytical methods. An effective procedure is Ethyl's Analytical Method EAM-54 entitled, "Determination of Trace Quantities of Copper in Gasoline." Copies are available on request.

An indirect method that may be used to advantage is the ASTM Induction Period Test, Method D 525-55. This test measures the increases in oxidation resistance achieved with varying dosages of "Ethyl" MDA. In some applications, soluble copper or metallic copper may be required in the test procedure.

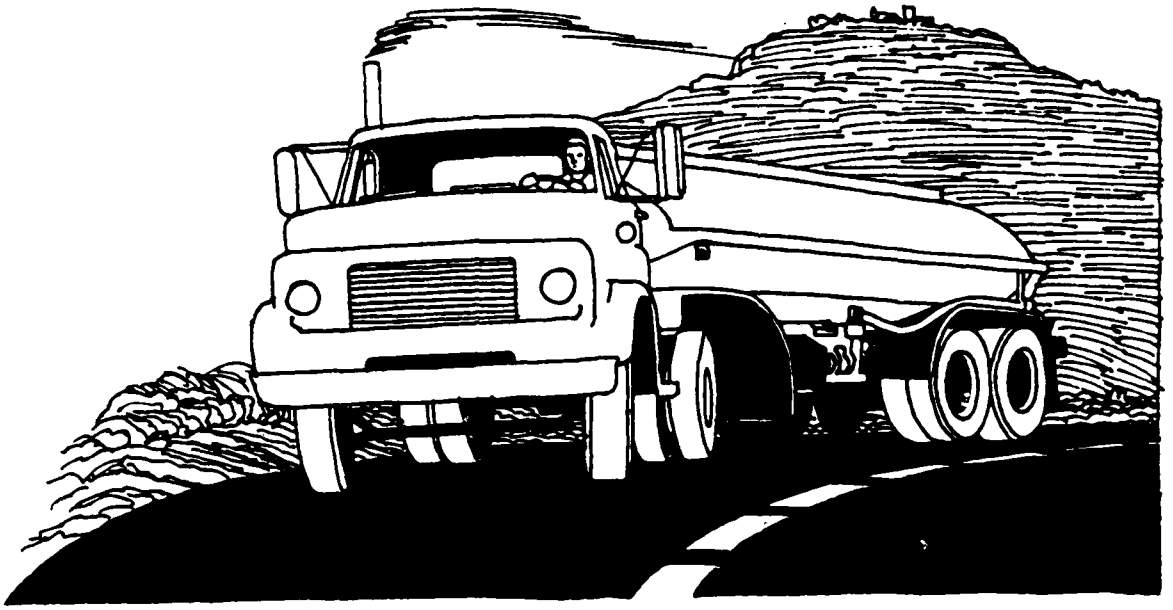
Blending

Since "Ethyl" MDA is made available as a solution in xylene, it is readily soluble in gasoline and distillate fuels at relatively low temperatures. Some blenders prefer to make stock blends by dissolving "Ethyl" MDA in another aromatic solvent, which will serve as the carrier for the other materials in the whole additive package.

"Ethyl" MDA should not be added to a fuel until after the final caustic wash, because it is subject to extraction by the caustic.

Military Motor Gasoline

Military Specification MIL-G-3056B requires a concentration of 1 to 3 lb/1000 bbl of a metal deactivator such as "Ethyl" MDA.



733-PDA, 733-PDA(D)

For Use In: Motor Gasolines, Aviation Gasolines, Jet Fuels.

"Ethyl" Antioxidants 733-PDA and 733-PDA(D) are physical mixtures of "Ethyl" Antioxidant 733 and the two diamine-type antioxidants. Three combinations are offered for each of the PDA's. These additive combinations provide effective antioxidants for gasoline where gum control is desired or inhibitor sweetening is practiced.

Solubility @ 68°F (20°C)	All PDA, PDA(D), and PDA(H) Mixtures
In Toluene	Miscible
In Water	Insoluble
In 10% Caustic	Insoluble
In Dilute Acid	PDA components soluble (see PDA's) 733 component insoluble

Physical Properties (Typical)

Composition, Wt %	733-PDA 75	733-PDA 50	733-PDA 25	733-PDA(D)75	733-PDA(D)50	733-PDA(D)25
733	75	50	25	75	50	25
PDA	25	50	75	-	-	-
PDA(D)	-	-	-	25	50	75
Form	← Liquid →					
Color	← Red →					
Density @ 68°F (20°C)						
g/ml	0.94	0.94	0.94	0.93	0.92	0.91
lb/U.S. gal.	7.8	7.8	7.8	7.8	7.7	7.5
Flash Point (COC), °F (°C)	252 (122)	259 (126)	270 (132)	73 (23)	71 (22)	67 (19)
(TCC), °F (°C)	92 (33)	116 (47)	180 (82)	46 (8)	46 (8)	50 (10)
Viscosity						
SUS @ 68°F (20°C)	201	201	173	79	67	60
cSt @ 40°C (104°F)	10.01	11.27	11.46	5.51	4.70	4.09
ISO VG (ASTM D 2422)	10	10	10	5	5	5
Freezing Point, °F (°C)	49 (9)	7 (−14)	34 (1)	60 (16)	40 (4)	15 (−9)

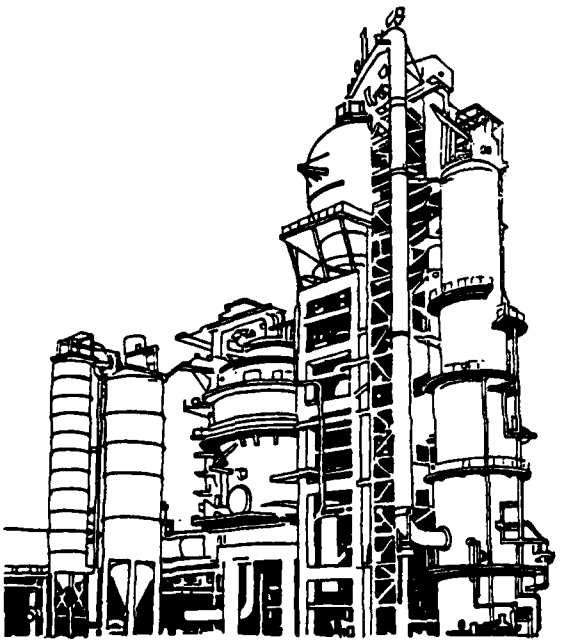
733-PDA(H)

For Use In: Motor Gasolines

"Ethyl" Antioxidants 733-PDA(H) are physical mixtures of "Ethyl" Antioxidant 733 and "Ethyl" PDA(H). The three combinations offered are effective antioxidants for motor gasoline where gum control is desired or inhibitor sweetening is practiced.

Physical Properties (Typical)

Composition, Wt %	733-PDA(H) 75	733-PDA(H) 50	733-PDA(H) 25
733	75	50	25
PDA(H)	25	50	75
Form	← Liquid →		
Color	← Red Amber →		
Density @ 68°F (20°C) g/ml	0.93	0.92	0.92
lb/U.S. gal.	7.8	7.7	7.7
Flash Point (COC), °F (°C)	220 (104)	238 (114)	285 (141)
(TCC), °F (°C)	148 (64)	179 (82)	225 (107)
Viscosity			
SUS @ 68°F (20°C)	211	318	398
cSt @ 40°C (104°F)	11.61	16.96	22.04
ISO VG (ASTM D 2422)	10	15	22
Freezing Point, °F (°C)	60 (15)	40 (4)	−5 (−21)



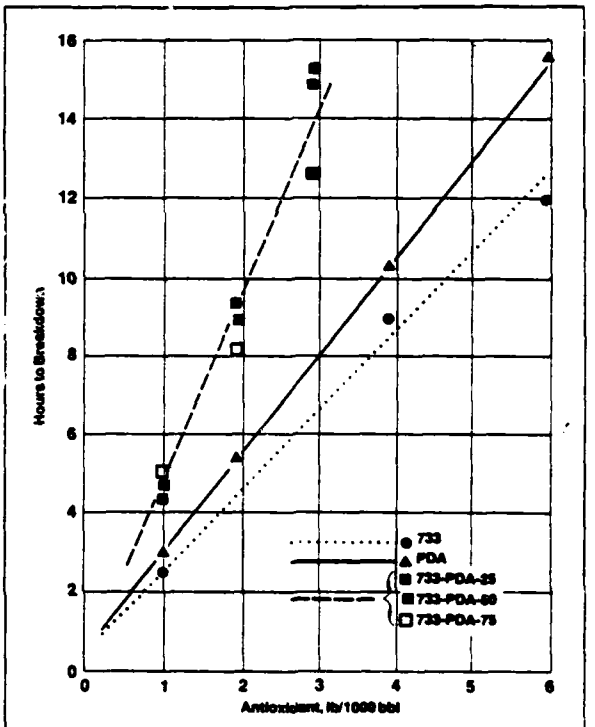
EVALUATION OF 733-PDA

"Ethyl" Antioxidant 733-PDA mixtures have been in use for 15 years. The following sections provide data comparing the performance of the mixtures to that of the two components. Two series of tests*—an oxygen bomb study and a 110°F storage evaluation—were conducted using an aviation alkylate containing TEL at 4.86 g Pb/U.S. gallon as 1-T fluid.

Bomb Tests

In the bomb tests, which were conducted using ASTM Method D 525 (IP-40), additive concentrations were studied over a range of 1-6 lb/1000 bbls. Additive effectiveness was measured as break point—the time in hours to change in slope of the oxygen absorption curve, indicating the start of TEL decomposition.

* Bartleson, J.D. and Shepherd, C.C., "How to Select Gasoline Antioxidants," *Hydrocarbon Processing*, 43, 153, August 1964.

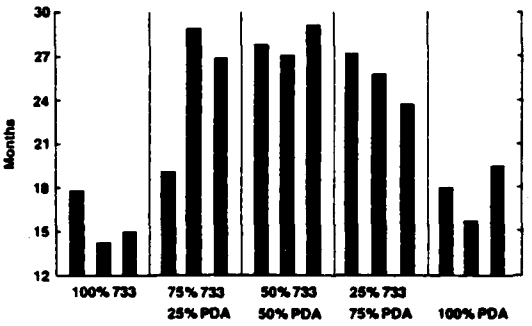


Oxygen Bomb Behavior of 733-PDA Mixtures
Aviation Alkylate (4.86g Pb/U.S. gal. as TEL)

As expected, "Ethyl" PDA performed slightly better than "Ethyl" 733. The unexpected result was that all three "Ethyl" Antioxidant 733-PDA mixtures—733-PDA 75, 733-PDA 50, and 733-PDA 25—outperformed "Ethyl" PDA by a significant margin at each additive concentration.

Storage Tests

Storage tests were conducted on the same additive combinations in the same fuel at a concentration of 1 lb/1000 bbl. SALS values were determined on the stored samples, and storage life was the time in months until a marked increase in TEL decomposition occurred (SALS value exceeded 4 mg Pb/100 ml.)



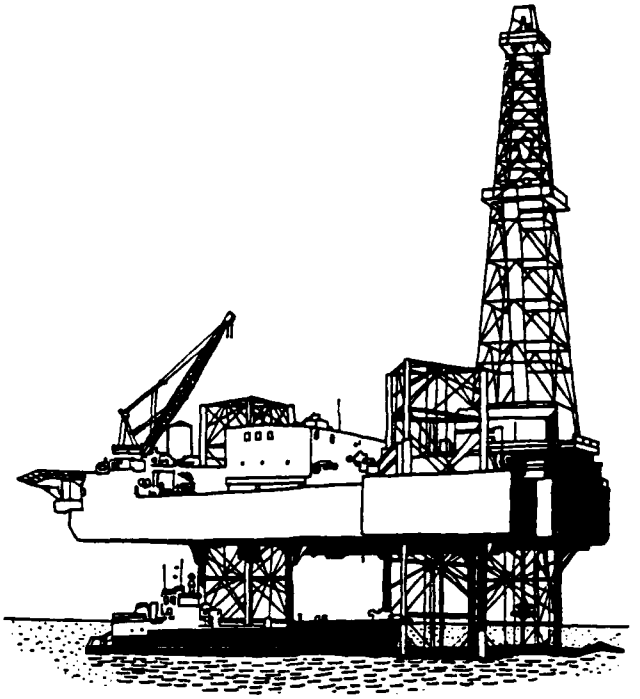
Storage Comparison of 733-PDA Mixtures
Months at 110°F to 4 mg Pb (as SALS)/100 ml
Leaded Aviation Alkylate (4.86g Pb/U.S. gal. as TEL)
+ 1 lb Antioxidant/1000 bbl

In the storage tests, "Ethyl" 733 gave storage life protection equivalent to that of "Ethyl" PDA. As observed in the bomb tests, however, the 733-PDA antioxidant mixtures outperformed the separate components by a factor of 2 to 1 regardless of the ratio of the two components in the mixture. "Ethyl" Antioxidant 733-PDA mixtures have performed successfully over many years in a large number of refineries.

Refinery Sweetening

A question frequently raised about the 733-PDA mixtures is their effectiveness in inhibitor sweetening. This is best answered by actual plant trials.

To compare the inhibitor sweetening effectiveness of "Ethyl" Antioxidant 733-PDA 50 to that of straight PDA, a refinery test was run in regular-grade gasoline in a large midwestern refinery at an additive concentration of 0.5 lb/1000 bbl. Samples were taken without additive treatment for a baseline comparison. The tests were run in January, with temperatures during the test period ranging from 0°F (-18°C) to 20°F (-7°C). Since lower temperatures slow down the sweetening reaction, this is a severe condition.



The tests were conducted by operating the refinery for several days on each additive and following the mercaptan analyses on storage tank samples of the finished gasoline blends at time intervals. The gasoline composition was:

	Volume %
Cat Cracked	48.7
Straightrun	18.4
Heavy Reformate	11.7
Light Reformate	6.0
C_5C_6 Gasoline	3.9
Light Cracked	3.4
Butane	7.9
	100.0

Initial mercaptan results varied for the four test fuels—two without antioxidant and two with antioxidants. One baseline fuel and the PDA-treated fuel had relatively low initial mercaptan levels of 0.0029 wt % mercaptan. The initial mercaptan values for the other two fuels were much higher—0.0059 wt % mercaptan for the second baseline and 0.0052 wt % for the 733-PDA 50 treated fuel.

The data below show mercaptan results after various storage times.

733-PDA 50 PLANT TRIAL

Mercaptan Content vs Storage Time

	Antioxidant		Wt % Mercaptan × 1000				
Fuel	Type	Conc., lb/1000 bbl	Initial	16 Hr	45 Hr	168 Hr	30 Days
A	None	0	2.9	-	1.8	1.4	0.8
B	PDA	0.5	2.9	1.1	-	0.8	0.6
C	733-PDA50	0.5	5.2	1.4	-	1.0	0.6
D	None	0	5.9	3.4	3.0	2.3	2.0

Even though the gasoline containing 733-PDA 50 had a much higher initial mercaptan content, the mercaptan levels for PDA and 733-PDA 50 were almost equal after 168 hours —0.0008 wt % for PDA and 0.0010 wt % for 733-PDA 50. Both gasolines met the refinery specification of 0.001 wt %. At 168 hours, the baseline fuels were off specification at 0.0014 wt % for Fuel A and 0.0023 wt % for Fuel D. Fuel D, the comparison fuel for 733-PDA 50, contained 0.002 wt % mercaptan sulfur after a 30-day storage period.

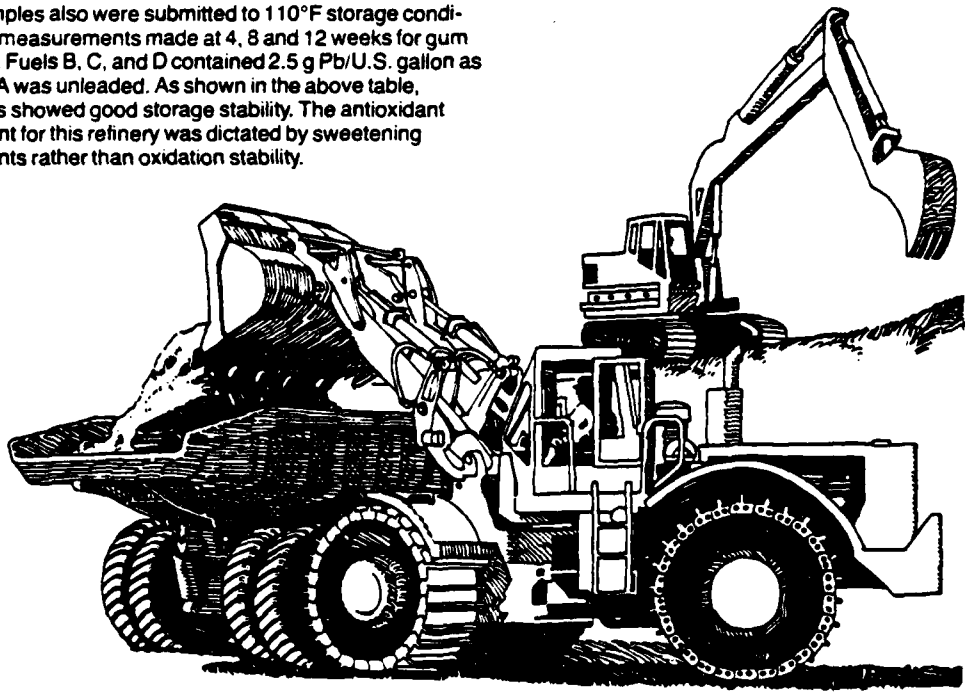
These results show that "Ethyl" Antioxidant 733-PDA 50 provided effective inhibitor sweetening equivalent to "Ethyl" Antioxidant PDA in a typical refinery operation under severe winter test conditions.

110°F Storage Data

	Antioxidant		Initial		4 Weeks		8 Weeks		12 Weeks	
Fuel	Type	Conc., lb/1000 bbl	Induction Period, minutes	ASTM Gum, mg/100 ml	ASTM Gum, mg/100 ml	SALS, mg Pb/100 ml	ASTM Gum, mg/100 ml	SALS, mg Pb/100 ml	ASTM Gum, mg/100 ml	SALS, mg Pb/100ml
A	None	0	915	1.8	1.4	<0.03 *	1.6	<0.03 *	1.8	<0.03 *
B	PDA	0.5	No Break	1.0	1.0	0.11	1.8	.08	2.0	0.14
C	733-PDA 50	0.5	1215	1.4	1.0	0.05	2.2	.06	2.0	0.09
D	None	0	960	1.0	1.2	0.07	1.2	.10	1.8	0.15

*Unleaded

These samples also were submitted to 110°F storage conditions, with measurements made at 4, 8 and 12 weeks for gum and SALS. Fuels B, C, and D contained 2.5 g Pb/U.S. gallon as TEL; Fuel A was unleaded. As shown in the above table, all samples showed good storage stability. The antioxidant requirement for this refinery was dictated by sweetening requirements rather than oxidation stability.



AVIATION GASOLINE TESTS

In another study, a number of additives at 4 and 8 lb/1000 bbl —PDA, PDA-D, 733, mixtures of 733 with PDA and PDA-D, and a commercial additive (60% 2, 4, di-*tert*-butylphenol + 40% mixed *tert*-butylphenols—Additive C on page 2)—were compared in a 115-145 aviation gasoline containing 4.86 g Pb/U.S. gallon as Aviation Mix. Tests conducted were ATSM Methods D 381 for existent gum and D 873 for 16-hour potential gum and precipitate; the maximum allowable results are 3 mg/100 ml existent gum, 6 mg/100 ml of 16-hour potential gum, and 2 mg/100 ml for 16-hour precipitate.

Composition	16-Hour Potential Gum, mg/100 ml	Precipitate, mg/100 ml	Existent Gum, mg/100 ml
Base Fuel (A)	2.5	0.0	2.6
A + 4.86g Pb/U.S. gal. Aviation Mix = B	44.9	57.1	2.0
B + 4 lb 733	1.1	0.0	2.4
B + 8 lb 733	1.8	0.0	1.4
B + 4 lb PDA(D)	1.3	0.0	0.8
B + 8 lb PDA(D)	1.6	0.0	0.8
B + 4 lb PDA	1.0	0.0	0.8
B + 8 lb PDA	1.4	0.0	0.8
B + 4 lb 733-PDA 50	1.2	0.0	2.0
B + 4 lb 733-PDA(D) 75	1.5	0.0	2.0
B + 4 lb 733-PDA(D) 50	1.6	0.0	2.4
B + Additive C	60.0	74.1	1.8

The leaded base fuel and the sample containing Additive C gave very poor results on potential gum and precipitate, with Additive C being even worse than the leaded base fuel. All of the other additives—733, PDA, PDA(D), and the 733 mixtures—were satisfactory. All of the fuels were subjected to 12-week storage tests for existent gum, precipitate, SALS, and peroxide number. All samples, including the base fuel, gave excellent results.

733-Toluene

These are combinations of "Ethyl" Antioxidant 733 and toluene blended to obtain low-temperature fluidity. They are for use in colder climates where it is desired to have a year-round liquid antioxidant for ease of handling.

Composition, Wt %	733-Toluene 80	733-Toluene 60
"Ethyl" Antioxidant 733 (Min.)	80	60
Toluene	20	40
Physical Properties (Typical)		
Form	Liquid	Liquid
Color	Yellow	Yellow
Density @ 68°F (20°C) g/ml	0.92	0.91
lb/U.S. gal.	7.7	7.6
Flash Point (TOC), °F (°C)	80 (27)	68 (20)
(TCC), °F (°C)	76 (24)	46 (8)
Freezing Point, °F (°C)	35 (2)*	10 (-12)
Viscosity		
SUS @ 68°F (20°C)	43	34
cSt @ 40°C (104°F)	2.46	1.42
ISO VG (ASTM D 2422)	2	2
Solubility @ 68°F (20°C)	Wt %	
In Toluene	Miscible	Miscible
In Water	Insoluble	Insoluble
In 10% NaOH	8 Max.	6 Max.
In 1% H_2SO_4	Insoluble	Insoluble

*Supercools

733-MDA

"Ethyl" Antioxidant 733-MDA is a physical mixture of "Ethyl" Antioxidant 733 and "Ethyl" Metal Deactivator. Three combinations are offered covering a range of product ratios. The additive combination provides economy in additive inventory and handling and insures the addition of the small concentration of metal deactivator normally used.

Composition, Wt %	733-MDA 80	733-MDA 67	733-MDA 50
"Ethyl" Antioxidant 733	80	67	50
"Ethyl" MDA, Total (80% Active plus 20% Xylene)	20	33	50
Physical Properties (Typical)			
Form	← Liquid →		
Color	← Amber →		
Density @ 68°F (20°C) g/ml	0.97	0.99	1.01
lb/U.S. gal.	8.1	8.2	8.4
Flash Point (COC), °F (°C)	216 (102)	187 (86)	167 (75)
(TCC), °F (°C)	108 (42)	80 (27)	68 (20)
Freezing Point, °F (°C)	55 (13)*	45 (7)*	35 (2)*
Viscosity			
SUS 68°F (20°C)	185	233	293
cSt @ 40°C (104F°)	9.87	12.86	17.76
ISO VG (ASTM D 2422)	10	15	15
Solubility @ 68°F (20°C)			
In Toluene	← Miscible →		
In Water	← Insoluble →		
In Caustic	733 component insoluble—see "Ethyl" Antioxidant 733. MDA component soluble.**		

* Supercools to much lower temperatures.

** MDA should not be added to a fuel until after the final caustic wash because it is subject to extraction by the caustic.

HANDLING AND BLENDING

"Ethyl" Antioxidants 701, 733, and 735 are chemically quite closely related. The major component of all three is 2, 6-di-*tert*-butylphenol, which is essentially the only compound in "Ethyl" 701. Thus, one can expect that use areas will overlap considerably.

Since "Ethyl" 701 is one compound, it has the highest and sharpest melting point at 97°F (36°C). Normally a solid, it may become partially or completely liquid when exposed to bright sunlight in warm climates.

Since "Ethyl" 733 and 735 are mixtures, they can exist partially liquid and partially solid over relatively broad temperature ranges. Both also have a tendency to "supercool" or remain liquid at temperatures below their freezing points. In other cases, they solidify completely, particularly when exposed to low temperatures for long periods, and warming to ambient temperature will not completely melt the products. If this situation is encountered, it is recommended that the contents be heated to at least 100°F (38°C) to melt the solids. Agitation will speed the melting process and assure homogeneity throughout the container.

It is good practice to occasionally check containers of "Ethyl" 733 and 735 for the presence of solids. This avoids discarding quantities of solid product that may adhere to the bottom or sides of containers. A complication sometimes encountered stems from the fact that such solids tend to be not only higher [illegible] effective antioxidants than the liquid portions. Thus, if the liquid portions are used in one batch of product and the solids in another, they may differ in their antioxidant effectiveness. Obviously, the best procedure is to use "Ethyl" 733 and 735 as homogeneous liquids.

"Ethyl" 701, 733, and 735 will withstand considerable exposure to air and heat without degradation providing high temperatures are not maintained for long periods. Electric drum blankets, hot rooms, or low-pressure steam are commonly used for melting.

APPROVALS

Specification	733	PDA	PDA(D)	PDA(H)	MDA	733-PDA	733-PDA(D)	733-PDA(H)	733-Toulene	733-MDA	701	735
For Motor Gasolines												
MIL-G-3056	●	●	●	●	●	●	●	●	●	●	●	●
For Aviation Gasolines												
MIL-G-5572	●	●	●			●	●		●		●	●
ASTM D-910 (Commercial)	●	●	●			●	●		●		●	
For Jet and Rocket Fuels												
MIL-T-5624 (JP-4, JP-5)	●				●				●	●	●	●
MIL-T-38219 (JP-7)	●	●			●	●				●	●	
MIL-T-83133 (JP-8)	●				●				●	●	●	●
MIL-F-25558 (USAF) (RAM Jet, RJ-1)	●	●			●	●			●	●		
MIL-P-25576 (Rocket Fuel, RP-1)	●	●			●	●			●	●		
MIL-F-25524 (Thermally Stable)		●			●	●			●	●	●	●
British D Eng. RD-2494	●				●				●	●	●	
ASTM D-1655 (Commercial)	●		●		●		●		●	●	●	●

ORDERING AND SHIPPING INFORMATION

SAFETY

Ordering Information		Contents of Container				Shipments		Freight Classification			DOT Classification			Other Hazardous Properties			
				Non-Returnable Steel Drums ICC Specification 17E		Rail	Truck							Toxic		Irritant	
		Tank Car	Tank Truck	55 Gallon (Tare 48 Lb.)	5 Gallon (Tare 5 Lb.)	Minimum Carload Lots	Min. Lots	Label	Rail	Motor	Flammable	Combustible	Corrosive	Dermal	Oral	Dermal	Eye
		Gallons	(1) Gallons	Net Lb.	Net Lb.	Drums	Drums										
701		6, 8 & 10,000		400	40	81	67	—									•
702		—		50(2)	—	(2)	(2)	—									
703		—		(3)	(4)	331	276	—									•
728		(5)	(5)	425	40	77	64	Combustible Liquid(6)				•				•	
733		6, 8 & 10,000		400	40	81	67	Flammable Liquid			•						•
735		6, 8 & 10,000		400	40	81	67	—									
PDA		Sizes on Request		425	40	85	71	Corrosive					•	•	•	•	•
PDA(D)				400	40	90	75	Flammable Liquid			•			•	•	•	•
PDA(H)				400	40	90	75	—						•			
733-PDA	75	6, 8 & 10,000		400	40	81	67	Flammable Liquid			•			•		•	•
	50	6, 8 & 10,000		425	40	77	64	Combustible Liquid(6)				•		•	•	•	•
733 PDA(D)	75	6, 8 & 10,000		400	40	81	67	Flammable Liquid			•			•			•
	50	6, 8 & 10,000		400	40	81	67	Flammable Liquid			•			•			•
733 PDA(H)	75	6, 8 & 10,000		400	40	81	67	Combustible Liquid(6)				•		•			•
	50	6, 8 & 10,000		425	40	77	64	Combustible Liquid(6)				•		•			•
733 Toluene	80	6, 8 & 10,000		425	40	77	64	Flammable Liquid			•				•		•
	60	6, 8 & 10,000		400	40	81	67	Flammable Liquid			•				•		•
733 MDA	80	6, 8 & 10,000		425	40	77	64	Combustible Liquid(6)				•					•
	67	6, 8 & 10,000		425	40	77	64	Flammable Liquid			•				•		•
	50	6, 8 & 10,000		450	40	73	61	Flammable Liquid			•				•		•
MDA	80	Sizes on Request		480	40	69	57	Flammable Liquid			•				•		•
	50	Sizes on Request		425	40	77	64	Flammable Liquid			•				•		•
HOA	44	6, 8 & 10,000		450	40	73	61	—								•	•
	22	6,8 & 10,000		425	40	77	64	Flammable Liquid			•					•	•

Gasoline or fuel additive containing less than 50% petroleum

Carbon, gum, or sludge removing compound NOT

Notes: Order and Shipping—Standard Container

(1) Tank cars on North American continent only. Tank trucks loaded to minimum applicable tariff weight. Any under loading penalty to customer's account.

(2) 50 Lb. bags are boxed in:

		Truck Lot	Carload Lot
Dual Pak	100 lbs. net	289	347
Quad Pak	200 lbs. net	146	175
M Pak	1,000 lbs. net (Palleted)	28	34
Ton Pak	2,000 lbs. net (Palleted)	15	18

24 gallon (100 lbs. net) Leverpak is a non-standard container

(3) Available in 24 gallon, Leverpak, tare 9 lbs., net 100 lbs.

(4) Available in 8 gallon Fibre Pak, tare 5 lbs., net 25 lbs.

(5) 728 is available in tank car, tank truck lots as custom oil blends.

(6) Combustible liquids are non-regulated in containers less than 110 gallon capacity.

Notes: Safety

(*) Contains toluene or xylene, thus considered toxic orally.

Precautionary Handling and First Aid

Flammable Keep away from heat sparks and open flame. Keep container closed. Use with adequate ventilation

Combustible Keep away from heat and open flame.

Corrosive (Causes Burns) Do not get in eyes, on skin, or on clothing. Avoid breathing vapor. Keep container closed. Use with adequate ventilation. Wash thoroughly after handling. *First Aid:* In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before re-use.

Toxic Dermally Avoid contact with eyes, skin, and clothing. Wash thoroughly after handling. *First Aid:* In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before re-use.

Toxic Orally Wash thoroughly after handling. *First Aid (for toluene and xylene-containing products):* If swallowed, do not induce vomiting. Call a physician immediately. *First Aid (others):* If swallowed, drink one or two glasses of water and induce vomiting by touching back of throat with finger or blunt object. Call a physician. Never induce vomiting or give anything by mouth to an unconscious person.

Eye and Skin Irritant Avoid contact with eyes, skin, and clothing. Wash thoroughly after handling. *First Aid:* In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before re-use.

Eye Irritant Avoid contact with eyes. Wash thoroughly after handling. *First Aid:* In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

Mail or Wire Orders:
Ethyl Corporation
Attention: P.C.D. Distribution Services
451 Florida, Baton Rouge, La. 70801

Telephone Orders:
Baton Rouge 504—388-7080

TWX Orders:
Teletype Directory Number
510—993-3597 (During working hours)

Telex Orders:
586-441
586-431

"ETHYL" LUBRICANT ADDITIVES PRICES

PRICE BULLETIN

Effective Date: December 15, 1979

PRODUCTS	*$/LB. F.O.B. ORANGEBURG, SOUTH CAROLINA			
	BULK	55 GALLON DRUMS		
	TC/TT	CL/TL	12 to TL	1 - 11
701	1.11	1.18	1.20	1.20
728	1.38	1.45	1.47	1.47
733	0.67	0.74	0.76	0.76
735	0.93	1.00	1.02	1.02

Minimum Tank Truck = 40,000 lbs. net

702	*$/LB. F.O.B. ORANGEBURG, SOUTH CAROLINA			
	TL (tariff min.)	2000 Lb. to TL	500 - 1900 Lb.	100 - 400 Lb.
TON-PAK	1.59	1.60	----	----
M-PAK	1.60	1.61	1.62	----
QUAK PAK or DUAL-PAK	1.61	1.62	1.63	1.67
DRUM	1.65	1.66	1.67	1.71

For terms and other information, see back.

Ethyl Corporation
Petroleum Chemicals Division
2 Houston Center • Suite 900 • Houston, Tex. 77002 • 713/654-4000
HOUSTON • NEW YORK • CHICAGO • TULSA • LOS ANGELES • CLEVELAND
PHILADELPHIA • KANSAS CITY • DALLAS • DENVER • SAN FRANCISCO

* Based upon availability of product. If shipments are made from Houston, Texas or Wilmington, California, add $0.04/pound or $0.07/pound respectively, except on products containing "Ethyl" Antioxidant 733, add $0.02/pound and $0.04/pound respectively.

Drum Loading (55-Gallon Drums) - Tare 48 Lbs.

Product	Net Wt. (Lbs.)
701	400
728	425
733	400
735	400
702 (24 gallon drum)	100

50 Lb. Bags

702		Net Wt. (Lbs.)	Nominal Tare Wt. (Lbs.)
Ton-Pak	(40 bags) - palletized	2,000	78
M-Pak	(20 bags) - palletized	1,000	64
Quad-Pak	(4 bags) - not palletized	200	7
Dual-Pak	(2 bags) - not palletized	100	5

TERMS:

Net 30 days or earlier at Ethyl's option. All orders subject to acceptance by Ethyl Corporation. Prices subject to change without notice unless protected by contract.

ORDERING INFORMATION:

Shipment of product may be most expeditiously handled by direct contact with our Distribution Services Group by mail, telephone, or wire.

MAIL OR WIRE:
Ethyl Corporation
Attn: PCD Distribution Services
451 Florida
Baton Rouge, La. 70801

TELEPHONE:
Baton Rouge:
504-388-7080

TWX or TELEX
Teletype:
510-993-3597
Telex:
586-441

"ETHYL" GASOLINE ADDITIVE PRICES

PRICE BULLETIN

Effective Date: December 15, 1979

PRODUCTS	*$/LB. F.O.B. ORANGEBURG, SOUTH CAROLINA			
	BULK	55 GALLON DRUMS		
	TC/TT	CL/TL	12/TL	1 - 11
733	0.670	0.740	0.760	0.760
MPA-447R	0.870	0.940	0.960	0.960
MPA-447RB	0.840	0.910	0.930	0.930
MPA-448	0.740	0.810	0.830	0.830
** MDA 80	3.400	3.440	3.450	3.450
** MDA 50	2.280	2.320	2.330	2.330
733-PDA 75	1.120	1.190	1.210	1.210
733-PDA 50	1.550	1.620	1.640	1.640
733-PDA-H 75	0.995	1.065	1.085	1.085
733-PDA-H 50	1.310	1.380	1.400	1.400
733-PDA-H 25	1.630	1.700	1.720	1.720
733-MDA 80	1.240	1.310	1.330	1.330
733-MDA 67	1.600	1.670	1.690	1.690
733-TOL 80	0.583	0.653	0.673	0.673
733-TOL 60	0.485	0.555	0.575	0.575

Minimum Tank Truck = 40,000 pounds net.
** F.O.B. Origin

PRODUCTS		$/LB. DELIVERED			$/Lb. FOB ORIGIN
		BULK (TC ONLY)	55 GALLON DRUMS		
			CL/TL	LTL 5 or More	LTL DRUMS 1 - 4
PDA	(1)	2.360	2.400	2.430	2.480
	(2)	2.410	2.450	2.480	2.480
PDA-D	(1)	1.610	1.650	1.680	1.730
	(2)	1.660	1.700	1.730	1.730
PDA-H	(3)	1.890	1.930	1.960	2.010
	(4)	1.940	1.980	2.010	2.010

For PDA's CL/TL = 30,000 lbs. net minimum load.
For terms, zones, and small containers, see back.

Ethyl Corporation
Petroleum Chemicals Division
2 Houston Center • Suite 900 • Houston, Tex. 77002 • 713/654-4000
HOUSTON • NEW YORK • CHICAGO • TULSA • LOS ANGELES • CLEVELAND
PHILADELPHIA • KANSAS CITY • DALLAS • DENVER • SAN FRANCISCO

(1) Continental U.S. except California, Oregon and Washington.
(2) California, Oregon, and Washington.
(3) East of Denver, Colorado.
(4) West of Denver, Colorado (Alaska not included).

* Based upon availability of product. If shipments are made from Houston, Texas or Wilmington, California, add $0.04/pound or $0.07/pound respectively, except on products containing "Ethyl" Antioxidant 733, add $0.02/pound or $0.04/pound respectively.

TERMS:

Net 30 days or earlier at Ethyl's option. All orders subject to acceptance by Ethyl Corporation. All prices are subject to change without notice unless protected by contract.

Drums Loading (55-Gallon Drums) - Tare 48 Lbs.

Product	Net Wt. (Lbs.)	Product	Net Wt. (Lbs.)
733	400	733-PDA 75	400
PDA	425	733-PDA 50	425
PDA-D	400	733-PDA-H 75	400
PDA-H	400	733-PDA-H 50	425
MPA-447R	400	733-PDA-H 25	425
MPA-447RB	400	733-MDA 80	425
MPA-448	400	733-MDA 67	425
MDA 80	480	733-TOL 80	425
MDA 50	425	733-TOL 60	400

30-Gallon Containers

Product	Net Wt. (Lbs.)
MDA 80	260
MDA 50	240

ORDERING INFORMATION

Shipment of product may be most expeditiously handled by direct contact with our Distribution Services Group by mail, telephone, or wire.

MAIL OR WIRE:	TELEPHONE:	TWX or TELEX
Ethyl Corporation	Baton Rouge:	Teletype:
Attn: PCD Distribution Services	504-388-7080	510-993-3597
451 Florida		Telex:
Baton Rouge, La. 70801		586-441

APPENDIX A

PART 3

Petrolite Corporation

PETROLITE CORPORATION

TRETOLITE DIVISION
369 Marshall Avenue / Saint Louis, Missouri 63119
(314) 961-3500 / TWX 910-760-1660 / Telex 44-2417

March 26, 1980

Mr. Robert Larson
USAE-WES-EE
P. O. Box 631
Vicksburg, MS 39180

Dear Mr. Larson:

As per your request, please find enclosed literature pertaining to Tretolite's Finished Product Additives.

Tretolite Industrial Price List is also enclosed for your reference file.

If additional information is required, don't hesitate to contact us.

Sincerely,

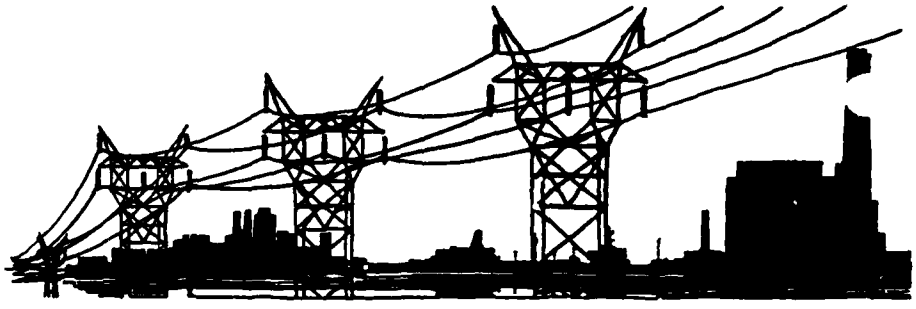
TRETOLITE DIVISION

H. S. Andrews, Jr.
Refinery Product Manager

HSA:jm

Enclosures

PETROLITE
TRETOLITE
DIVISION
Saint Louis, Missouri 63119
(314) 961-3500
London NW3 6JE, England
(01) 586-1251



TRETOLITE PRODUCTS FOR INDUSTRIAL FUELS

KONTOL* KI-16

Vanadium Corrosion Inhibitor Additive

DESCRIPTION

KI-16 is a liquid, oil-soluble, organo-magnesium fuel additive for vanadium inhibition in crude oil and residual grade fuel oils. It is particularly recommended to combat high-temperature vanadium corrosion in industrial gas turbines designed to operate on heavy fuels. KI-16 meets turbine manufacturer's additive specifications. KI-16 provides a minimum eight percent active magnesium in a non-abrasive and ready-to-use, highly soluble form. The controlled low trace-metal level of KI-16 allows high dosage without additional contamination in fuels containing significant amounts of vanadium.

APPLICATION

Add KI-16 directly to nearly ash-free gas turbine liquid fuels such as grades 2-GT and 3-GT, with minor vanadium contamination. In other low to high ash-bearing fuels requiring sodium and potassium reduction to specification levels, KI-16 is added after water-washing and fuel purification by electrostatic or centrifugal techniques. Add KI-16 to circulated warm fuel and assure adequate mixing by magnesium analysis. Completely oil-soluble, KI-16, when pre-mixed with stored clean fuel, does not degrade, settle out or stratify.

DOSAGE

Use a minimum of 37.5 ppm of KI-16 (by weight) for each ppm of vanadium present in the fuel. This will maintain the turbine manufacturer's recommended 3-to-1 magnesium to vanadium treating ratio.

TYPICAL PROPERTIES

Form	Clear dark liquid
Density, lbs./gal.	9.25
Pour point, °F	−20
Particle size, μ 99.9%	<2
Sediment, %	<0.05
Viscosity SUS, 100°F	950
Viscosity SUS, 60°F	2500
Viscosity SUS, 30°F	6000
Flash point, TOC, °F	>150
Flash point, PMCC, °F	>120

STORAGE AND HANDLING

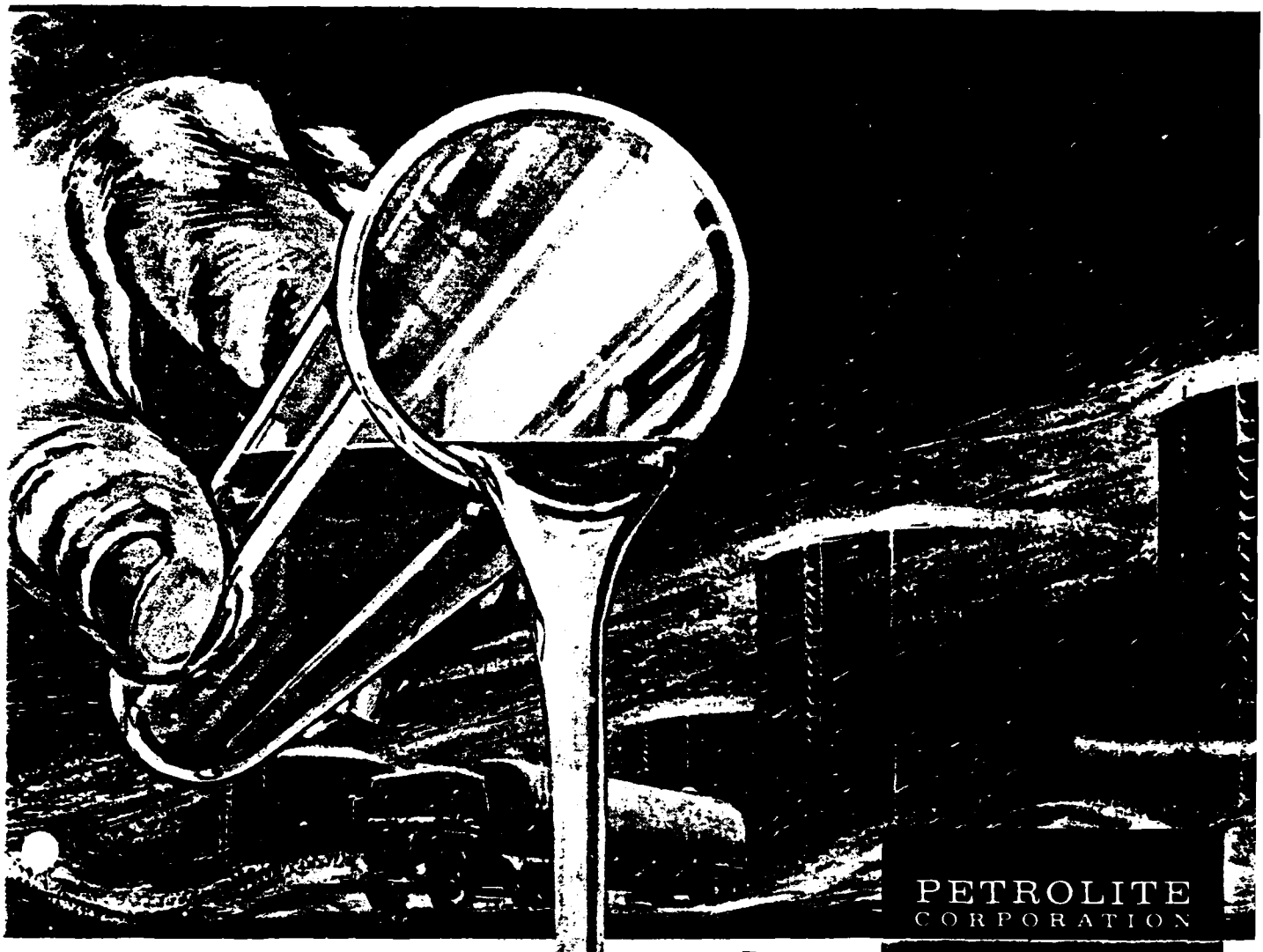
KI-16 is readily pumpable from unheated additive storage at temperatures above 32°F. it is stable in mild steel and aluminum storage tanks or in original containers over long periods of time.

KI-16 is an industrial chemical and should be handled with the same precautions as used with ordinary distillates, solvents, and weak alkalis. Avoid open flame. Avoid skin and eye contact. Wash contaminated areas with soap and water.

AVAILABILITY

KI-16 is supplied in bulk quantities and in net 55-U.S. gallon, non-returnable steel drums (550 pounds gross, 510 pounds net weight). Shipping Classification: "Compound, Crude Petroleum Treating".

Tretolite Division sales offices and warehouses are located in major petroleum producing centers.



TRETOLITE
DIVISION

369 Marshall Avenue, St. Louis, Missouri 63119

TOLAD® Cold Flow Improvers

for middle distillate fuels

A-123

TOLAD®

Cold Flow Improvers

...the answer
to winter handling
and storage problems

TOLAD* Cold Flow Improvers are controlled-structure polymer compositions in aromatic hydrocarbon solvents. They provide an economical means of improving the low temperature handling properties of middle distillate fuels without adversely affecting fuel stability and water tolerance.

WHY THEY ARE USED

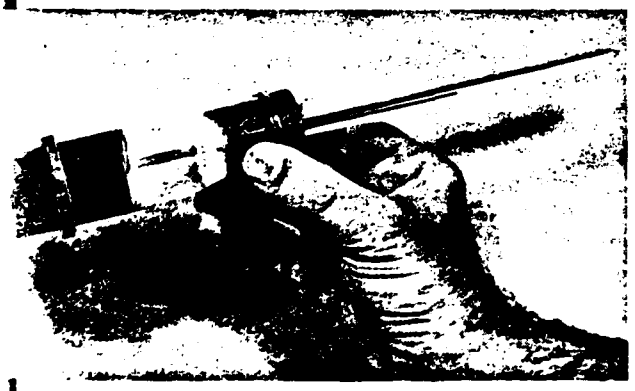
Heating oils and diesel fuel contain wax portions which can separate and crystallize during exposure to cold climates. The wax crystals form a lattice structure which restricts fuel flow through filters and lines and can eventually solidify the entire fuel mass, causing clogging problems for the refiner, distributor, or consumer.

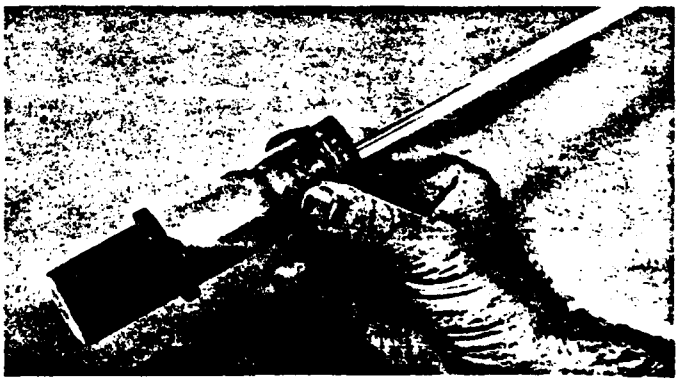
TOLAD Cold Flow Improvers modify the natural wax crystal formation pattern, thereby preventing the growth of large, troublesome crystals during winter storage and handling.

Historically, kerosene has been blended with other fuel components to lower the pour point and keep fuel fluid in cold weather. Often, however, fuels may require costly kerosene blending for frigid climates. When kerosene is needed for jet fuel and other more profitable blending operations, it is uneconomical to downgrade it to heating oil.

By providing flexibility in refining operations, the use of TOLAD Cold Flow Improver aids the refiner

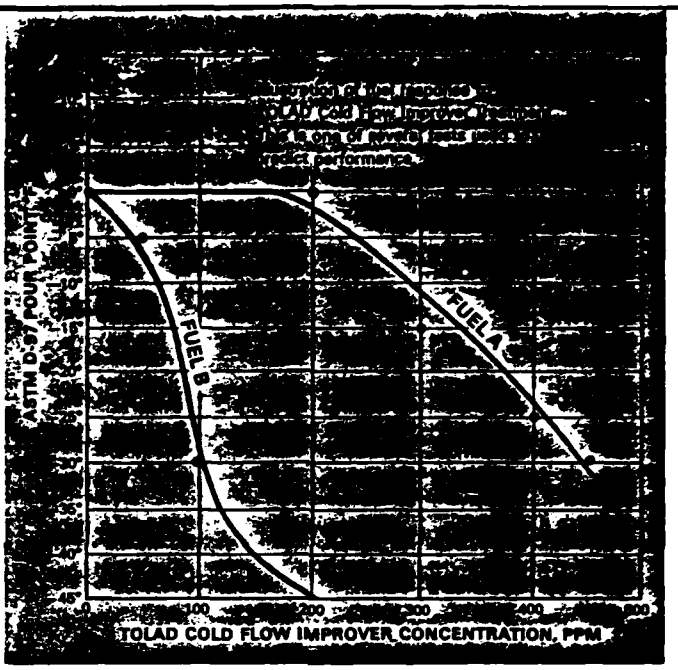
TOLAD Cold Flow Improvers (right) enable fuel to flow. At the same temperature untreated fuel (left) is solidified.





*Registered Trademark, Petrolite Corporation

Cold flow improvers are evaluated for their efficiency in improving the fluidity of fuel samples at low temperatures.



in matching fuel component inventories with their most profitable end use.

TOLAD Cold Flow Improvers are supplied in drums, tank truck, or tank car.

APPLICATION

TOLAD Cold Flow Improvers should be added to fuels at temperatures above their cloud point. Addition can be made any place in the fuel distribution system where adequate mixing will be obtained. The required additive concentration depends upon the expected weather severity in the geographical marketing area and upon the response of the particular fuel blend to additive treatment. Commonly, 50 ppm to 500 ppm will satisfy most field requirements.

Testing to measure fuel pumpability at low temperatures. One aspect of cold flow improver additive study.

Determining Additive Requirements

Laboratory testing is suggested to determine approximate additive requirements for a particular fuel blend. No one lab test can accurately simulate all actual field environment conditions. The Tretolite laboratory therefore employs testing to measure effects on pour point, fluidity, and pumpability, then correlates this information with the refiner's previous laboratory and field experience.

STORAGE

TOLAD Cold Flow Improvers, liquid at room temperature, should be stored indoors or diluted with aromatic hydrocarbon to maintain pumpability. Dilution also fosters quick, efficient distribution in the fuel.

TECHNICAL SERVICE

Your nearby Tretolite service engineer, backed by Petrolite's extensive research facilities and testing laboratories, stands ready to assist you in obtaining maximum performance and economy from TOLAD Cold Flow Improvers. Ask the Man in the Red Car about your particular application.

PETROLITE
CORPORATION

TRETOLITE DIVISION

TOLAD-31
Cold Flow Improver

Description:

TOLAD-31 Cold Flow Improver is a completely organic, ash free pour point depressant designed for use in crude oil, heavy fuel oils and gas oils.

Application:

TOLAD-31 reduces the natural pour point of waxy crude and heavy oils allowing them to be stored, handled and transported without having to use and maintain expensive heating devices or diluents. A typical application is in the storage and transportation of cat cracker feedstock where TOLAD-31 is being used to lower the pour point by 50°F. or more. Since TOLAD-31 functions by modifying wax crystal formation, it should be added when the fuel is warm (prior to wax formation). Typical use rates are 200 to 4000 ppm depending on the properties and response of the actual fuel. Simple laboratory tests can be conducted to determine adequate use rates.

Typical Physical Properties:

Form: Amber-brown viscous liquid.
Specific Gravity: 0.893
Weight: 7.45 pounds/gallon

Viscosity:

Temp. °F.	SUS	CS
60	50.8	7.6
100	41.4	4.7
130	37.3	3.4

Pour Point: 20 - 30°F.
Flash Point, TOC: 125°F.

Handling:

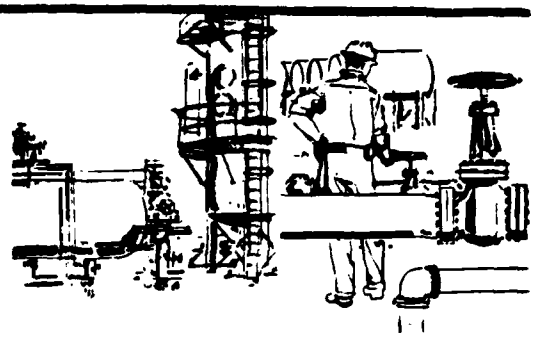
TOLAD-31 is not considered a toxic substance, but should be handled with the same precautions used for industrial solvents. The product has been designed for easy handling and injection.

Availability:

TOLAD-31 is supplied in 55-gallon nonreturnable steel drums, approximately 440 pounds gross weight, and also in bulk quantities.

Shipping classification is "Compound, crude petroleum treating".

PETROLITE CORPORATION
TRETOLITE DIVISION
Saint Louis, Missouri 63119 / (314) 961-3500



TRETOLITE PRODUCTS FOR PETROLEUM REFINERS

TOLAD® T-35 Cold Flow Improver

GENERAL DESCRIPTION

TOLAD T-35 is a controlled structure polymer composition in aromatic hydrocarbon solvent. TOLAD T-35 improves the cold flow characteristics of middle distillate fuels by modifying the wax crystal structure.

RECOMMENDED USE

The flexibility and economics of fuel blending operations can be greatly improved by using TOLAD T-35 to achieve the desired cold weather fuel handling properties. For example, fuel component percentages can be altered and/or end points changed. Changes can be made to reflect the cost or price of the fuel blend components or to imrpove fuel quality. TOLAD T-35 can be used economically to overcome any deterioration of cold flow properties resulting from these changes.

Fuel cold flow properties can be evaluated in the laboratory by procedures such as the pour point, fluidity, and pumpability tests. Typically, 50 to 500 ppm of TOLAD T-35 is used depending upon the fuel and the flow properties desired. For example, the pour point of a fuel may be lowered by up to 50°F. or more through the use of TOLAD T-35.

APPLICATION

TOLAD T-35 can be added to fuels at any point in the fuel distribution system, however, maximum efficiency is obtained when the addition is made to warm fuel. Wax crystals grow in middle distillate fuels as their temperature decreases. The addition of cold flow improver to hot or warm fuel allows the additive to be present during the early growth of the wax crystals. The addition of additive to cool fuel may result in poor treating efficiency. Addition of TOLAD T-35 near the cloud point of the fuel is of minimum benefit. Continuous injection is more effective than batch treatment.

Cold flow improvers are often diluted in a mix tank prior to injection in the fuel stream. Recommended diluents for TOLAD T-35 are aromatic materials such as reformate. TOLAD T-35 is not completely soluble in some hydrocarbons at the 10% to 50% dilutions used in mix tanks. If a suitable diluent is not available or another diluent is preferred, a mixer or simple recirculation pump can be employed. TOLAD T-35 is completely soluble in fuels at use concentrations.

COMPATIBILITY

TOLAD T-35 in fuel strength is compatible with other pour point depressant additives and most fuel oil stability additives. If TOLAD T-35 is to be mixed in a storage tank with another additive, prior to injection, their compatibility should be investigated before mixing them. Separate injection may be necessary in some cases.

The compatibility of TOLAD T-35 and other fuel additives has been investigated at use concentration in fuels. No detrimental effects were observed. Other additives continued to function, for example, as rust inhibitors, fuel degradation inhibitors, dispersants, etc., in the presence of TOLAD T-35. When tested alone, TOLAD T-35 shows no effect on a fuel's corrosiveness or stability.

Continued

WATER TOLERANCE

Fuels containing TOLAD T-35 have been evaluated on many types of laboratory tests designed to determine the ability of a fuel to shed water. Several fuel/water ratios and methods of mixing the fuel and water have been investigated to simulate the various conditions encountered in fuel storage and transportation systems. Samples containing TOLAD T-35 perform essentially the same as those containing no additive.

HANDLING

TOLAD T-35 contains aromatic solvent and should therefore not be allowed to remain in contact with the skin nor should contaminated clothing be worn for a prolonged period. Eyes should be protected. In case of accidental splashing on the skin, wash with soap and water.

TYPICAL PHYSICAL PROPERTIES

Density, Lb./Gal @ 60°F	7.83
Flash Point, SFCC, °F	112
Pour Point, ASTM D-97, °F	40
Viscosity, SUS, @ 130°F	115
Viscosity, @ 100°F	220
Viscosity, @ 80°F	304
Ash	Nil

AVAILABILITY

TOLAD T-35 is available in 55-gallon drums and in tank truck bulk quantities.

PETROLITE CORPORATION
TRETOLITE DIVISION
300 Marshall Avenue / Saint Louis, Missouri 63119
(314) 961-3500 / TWX 910-760-1660 / Telex 44-2417

TOLAD COLD FLOW IMPROVER 37

GENERAL DESCRIPTION

TOLAD 37 is a blend of 30%v TOLAD 35 and 70%v aromatic solvent. This dilution was commercialized to produce a product which could be stored and easily handled under cold climatic conditions.

RECOMMENDED USE

TOLAD 37 improves the cold flow characteristics of middle distillate fuels by modifying the wax crystalline structure. By using an additive, rather than kerosene, to maintain desired cold weather fuel handling properties, flexibility and economics of operation can be greatly improved. In most fuels, the improvement in cold flow properties is proportional to additive concentration. Typically 150 to 1500 ppm of TOLAD-37 is used depending upon the lowest ambient temperatures anticipated.

Fuel cold flow properties can be estimated in the laboratory by pour point, fluidity and pumpability type test procedures.

APPLICATION

TOLAD 37 can be added to fuels at any point in the fuel distribution system, however, maximum efficiency is obtained when the addition is made to warm fuel. Wax crystals grow in middle distillate fuels as their temperature decreases. The addition of cold flow improver to hot or warm fuel allows the additive to be present during the early growth of the wax crystals. The addition of additive to cool fuel may result in poor treating efficiency. Addition of TOLAD 37 near the cloud point of the fuel is of minimum benefit. Continuous injection is more effective than batch treatment.

TYPICAL PHYSICAL PROPERTIES

Weight	7.5 lb./gal.
Flash Point	above 110°F.
Pour Point	below -45°F.
Viscosity @ 0°F.	75 SUS
" @ -20°F.	120 SUS
" @ -30°F.	155 SUS

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TOLAD-61

DESCRIPTION

TOLAD-61 is a completely organic, ash free heavy oil cold flow improver in an aromatic solvent. TOLAD-61 decreases the pour point of waxy gas oils, heavy gas oils, heavy fuel oils and topped crudes by modifying the wax crystal structure.

RECOMMENDED USE

TOLAD-61 is recommended to improve the cold flow properties of heavy gas oils and heavy fuel oils. Generally, TOLAD-61 has greatest activity in distilled products which have high wax content.

APPLICATIONS

TOLAD-61 will reduce the pour point of gas oils, heavy catalytic cracker feeds and distilled fuels by modifying the crystal structure to induce the formation of small isotropic crystals. A typical application of TOLAD-61 is pour point depression of a heavy catalytic cracker feed from a +75°F. natural pour to a +40°F. pour thereby allowing a refiner to pipe line the cat cracker feed from one refinery to another. TOLAD-61 will also reduce the pour point of #6 heavy distillate 40°F. to a sales specification of +55°F.

COMPATIBILITY

TOLAD-61 is compatible with all hydrocarbons and fuels particularly aromatic fuels. It is compatible with other cold flow improvers and fuel additives.

TYPICAL PHYSICAL PROPERTIES

Weight	7.1 lbs./gal. @ 130°F.
Flash Point (SFCC)	above 130°F.
Melt Point	100°F. - 105°F.
Viscosity	145 SUS @ 130°F. 70 SUS @ 212°F.
Ash	Nil

PETROLITE
CORPORATION

TRETOLITE DIVISION

TOLAD T-260
Fuel Stability Additive

General Description:

TOLAD T-260 is an ashless organic multifunctional distillate fuel oil additive. TOLAD T-260 reduces residue formation, inhibits color degradation and effectively disperses sludge to prevent plugging of filters, strainers, and nozzles.

Use Concentration:

The concentration of TOLAD T-260 used depends upon the nature of the fuel and the fuel quality desired. With TOLAD T-260, up to 90% reduction in the formation of filterable residue can be obtained in a wide range of fuels. It is recommended that TOLAD T-260 be added on a continuous basis to fuel blends or to a selected fuel blend component stream.

Typical Physical Properties:

Density, Lbs./Gal. @ [illegible]	7.5
Flash Point, SFCC, °F.	126
Pour Point, ASTM D-97, °F.	-40
Viscosity, SUS, @ 0°F.	5,859
@ 30°F.	1,257
@ 60°F.	438

Handling:

In handling TOLAD T-260, proper precautions common to most hydrocarbons should be taken. Avoid open flame. Avoid skin and eye contact. Wash contaminated areas with soap and water.

Availability:

TOLAD T-260 is available in 55-gallon nonreturnable steel drums and in tank truck bulk quantities.

PETROLITE
CORPORATION

TRETOLITE DIVISION

TOLAD T-316
Sludge Dispersant for Fuel Oils

General Description:

TOLAD T-316 is a liquid, oil-soluble dispersant additive for fuel oils. It is recommended as a pre-combustion oil additive to eliminate sludge separation and deposit plugging of fuel lines, filter strainers, preheaters and burner tips as is often encountered in handling residual fuels containing sludge.

All petroleum oils exhibit sludging tendencies in storage. This is due to oxidation and polymerization reactions and the eventual precipitation of such insoluble derivatives as gums, resins, asphaltenes and sediments. Small amounts of water present in the fuel can also contribute to emulsification and the eventual settling of a thick, troublesome sludge deposit in the storage tank and fuel lines.

TOLAD T-316 added to the fuel acts to solubilize and prevent the sludge separation and stratification. The additive keeps the fuel contaminants uniformly well dispersed for good fuel atomization and clean, deposit free burning.

Typical Physical Properties:

Appearance	Dark Amber Liquid
Density, Lbs./Gal. @ 60°F.	7.84
Flash Point, SFCC, °F.	141
Pour Point, ASTM D-97, °F.	-5
Viscosity, SUS, @ 0°F.	964
@ 30°F.	320
@ 60°F.	140

Application:

TOLAD T-316 is a ready to use liquid and is easily mixed into fuel storage tanks with circulation or upon fuel delivery. In heavy oils such as Bunker C, use one gallon TOLAD T-316 to 4,000 gallons of fuel oil to disperse existing sludge deposits. Reduce concentration 1 to 5,000 to keep sludge well dispersed. Light fuel oils may require as little as 1 to 10,000 to maintain a clean system. Tretolite Sales Engineers will provide specific recommendations for each system.

Handling:

TOLAD T-316 stored in sub-freezing outside areas may require warming for good pourability. TOLAD T-316 is an industrial chemical and should be handled with the same precautions as used with ordinary distillates and petroleum solvents. Avoid open flame. Avoid skin and eye contact. Wash contaminated areas with soap and water.

Availability:

TOLAD T-316 is supplied in bulk and in net 55 U.S. gallon, nonreturnable steel drums (475 pounds gross, 435 pounds net weight) from Tretolite Division, Petrolite Corporation, 369 Marshall Avenue, St. Louis, Missouri 63119. Telephone: 314/961-3500. Shipping Classification: "Compound, Crude Petroleum Treating"

PETROLITE
CORPORATION

TRETOLITE DIVISION

X-CIDE Industrial Bactericide
XC-320

General Description:

X-CIDE 320 is a brine soluble, liquid polyamine, semi-polar compound possessing excellent corrosion and bacterial properties.

Recommended Use:

X-CIDE 320 is recommended for use in non-potable type industrial water systems where bacterial slime and corrosion problems exist. Examples of industrial applications are industrial recirculating water cooling systems, oil field and petrochemical water injection systems; oil field producing systems, tanks and disposal systems where the effluent does not drain into streams, lakes, ponds or municipal water systems. X-CIDE 320 is designed to control both aerobic and anaerobic types of bacteria and algae and fungi. Of the aerobic types, it is particularly recommended for the control of so-called "iron bacteria". XC-320 is very effective in controlling the anaerobic "sulfate reducing" bacteria that are responsible for producing large quantities of hydrogen sulfide.

Treatment Recommendations:

The Tretolite representative will make a specific recommendation for your system. The following are typical treatment schedules:

<u>Oil Field and Petrochemical Systems</u>:

X-CIDE 320 may be used either in slug treatment or in continuous application. Dosages may vary from 500 ppm of X-CIDE 320 in slug application to 30-50 ppm of X-CIDE 320 in continuous treatment. (¼ pint per 1000 gallons equals approximately 30 ppm.) A typical slug treatment is to add 120 ppm of X-CIDE 320 (1 pint per 1000 gallons of water) at intervals as needed to prevent growth of bacterial slime. Badly fouled systems may be slug treated to establish control, followed by continuous treatment of 30-60 ppm (¼ to ½ pints per 1000 gallons of water) to maintain control.

Industrial Recirculating Water Cooling Systems:

Dosages for recirculating water cooling towers or evaporative condensors will depend on the condition of the system prior to treatment. Systems which are heavily fouled should be cleaned first. Apply X-CIDE 320 to the cleaned system when regrowth is first noticed according to the following schedule:

Initial Dose: Apply 120 ppm of X-CIDE 320 (1 pint per 1000 gallons of water) in the system. Repeat the dose once, twice or three times a week until control of growth is established.

Subsequent Dose: When control is evident on a continuous basis, add sufficient X-CIDE to maintain 30 to 50 ppm into the blowdown water (4 to 7 fluid ounces per 1000 gallons of water).

Apply X-CIDE 320 at a point in the system where it will be uniformly mixed.

As a corrosion inhibitor, X-CIDE 320 is equally effective as it is a bactericide in preventing acid or saline corrosion attack.

Typical Physical Properties:

Specific Gravity	0.963
Weight Per Gallon	8.02
Flash Point, TOC	117°F.
Pour Point	Below -20°F.

Shipping:

X-CIDE 320 is shipped in 55-gallon steel drums, F.O.B. St. Louis, Missouri or Brea, California.

Handling:

X-CIDE 320 is an industrial chemical and all the normal precautions used in handling industrial chemical should be observed. See label for First Aid instructions.

EPA Registration Number 5009-4

PETROLITE
CORPORATION

TRETOLITE DIVISION

X-CIDE Industrial Bactericide
XC-370

GENERAL DESCRIPTION:

X-CIDE 370 is a water-soluble liquid, organic nitrogen bactericide.

RECOMMENDED USE:

X-CIDE 370 is recommended for use in those industrial, non-potable waters where a bacterial problem is clearly demonstrated. Examples of X-CIDE 370 applications are as follows: disposal water systems where the effluent does not drain into lakes, streams, ponds or public water supplies; water injection systems from petrochemical and oil field operations and cooling water recirculating systems. X-CIDE 370 will control both aerobic and anaerobic type bacteria. X-CIDE 370 is very effective in controlling the anaerobic "sulfate reducing" bacteria that are responsible for producing hydrogen sulfide. Recommended dosage for slug treatments (the preferred treatment method) may be as high as 500 ppm. Bacterial control may be maintained by use of 30 - 50 ppm of X-CIDE 370 on a continuous basis, (1/4 pint per 1000 gallons equals approximately 30 ppm).

TYPICAL PHYSICAL PROPERTIES:

Specific Gravity, 60°F	0.930 to 0.945
Lbs./Gallon, 60°F	7.75 to 7.87
Flash Point, SFCC	75°F (Min.)
Pour Point, (ASTM D-97)	-10°F
Viscosity, 0°F	1020 SUS
" 30°F	340 SUS
" 60°F	155 SUS
" 100°F	58 SUS

HANDLING:

X-CIDE 370 is an industrial chemical and all the precautions taken in handling industrial chemicals should be observed.

SHIPPING:

X-CIDE 370 is shipped in a 55-gallon steel drum, F.O.B. St. Louis, Missouri or Bree, California.

FIRST AID:

First Aid instructions are stated on the drum label.

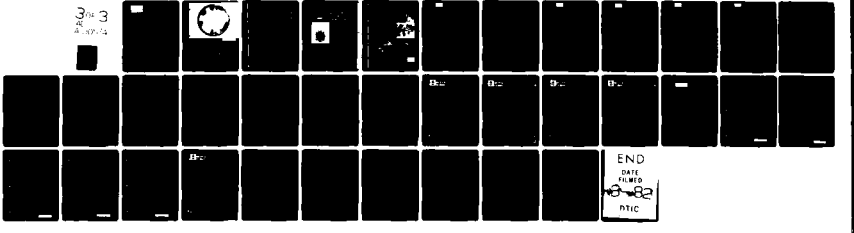
OCT., 1978

EPA Registration No. 5009-8.

"The information contained in this technical bulletin is, to the best of our knowledge, true and accurate, but Petrolite Corporation disclaims any liability with respect to any recommendations or suggestions made in connection therewith. There are no warranties which extend beyond the description on the face hereof."

April, 1979

AD-A110 574 ARMY ENGINEER DIV HUNTSVILLE AL F/G 15/5
ADDITIVES TO PREVENT DELETERIOUS EFFECTS ASSOCIATED WITH LONG-T--ETC(U)
SEP 80 R J LARSON, P G MALONE
UNCLASSIFIED HNDTR-80-50-SP NL



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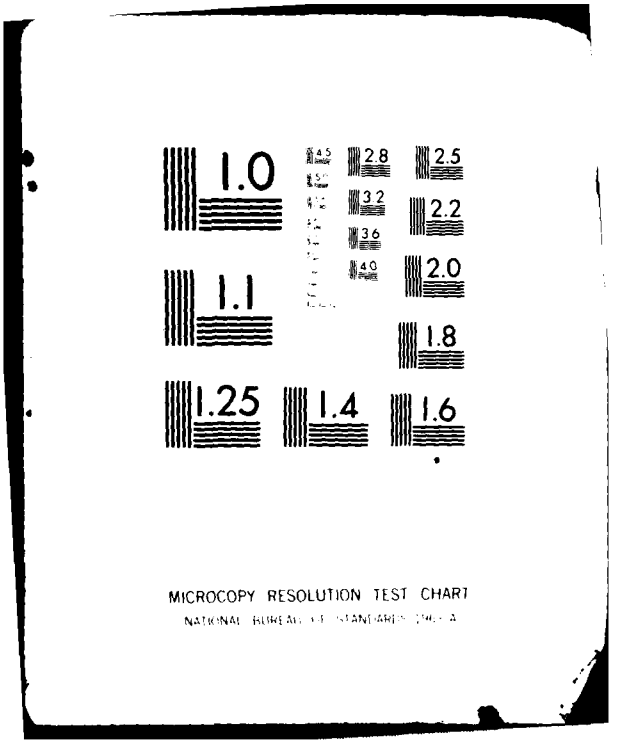
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MICROCOPY RESOLUTION TEST CHART

PETROLITE
CORPORATION

TRETOLITE DIVISION

X-CIDE Industrial Bactericide
XC-401

General Description:

X-CIDE-401 is a blend of bactericidal diamines and poly-chlorinated phenolic compounds.

Recommended Use:

X-CIDE-401 is particularly recommended for the control of bacterial growths in high brine or industrial, non-potable, fresh waters. X-CIDE-401 is highly effective in controlling the anaerobic bacteria that produce hydrogen sulfide as well as the aerobic bacteria present in waters. Examples of XC-401 applications are as follows: disposal water systems where the effluent stream does not drain into streams, lakes, ponds or municipal water systems; petro-chemical and oil field water injection systems and cooling water recirculating systems. Treatment dosages may be as high as 500 ppm in slug type applications to 30 - 50 ppm (1/4 of a pint in 1000 gallons equals approximately 30 ppm) in a continuous application. A typical slug application is 120 ppm (1 pint per 1000 gallons).

Typical Physical Properties:

Weight, 60°F., Lbs./Gal.	8.75
Flash Point, TOC	120°F.
Pour Point	-15
Viscosity, SUS, 100°F.	49
Viscosity, SUS, 130°F.	40

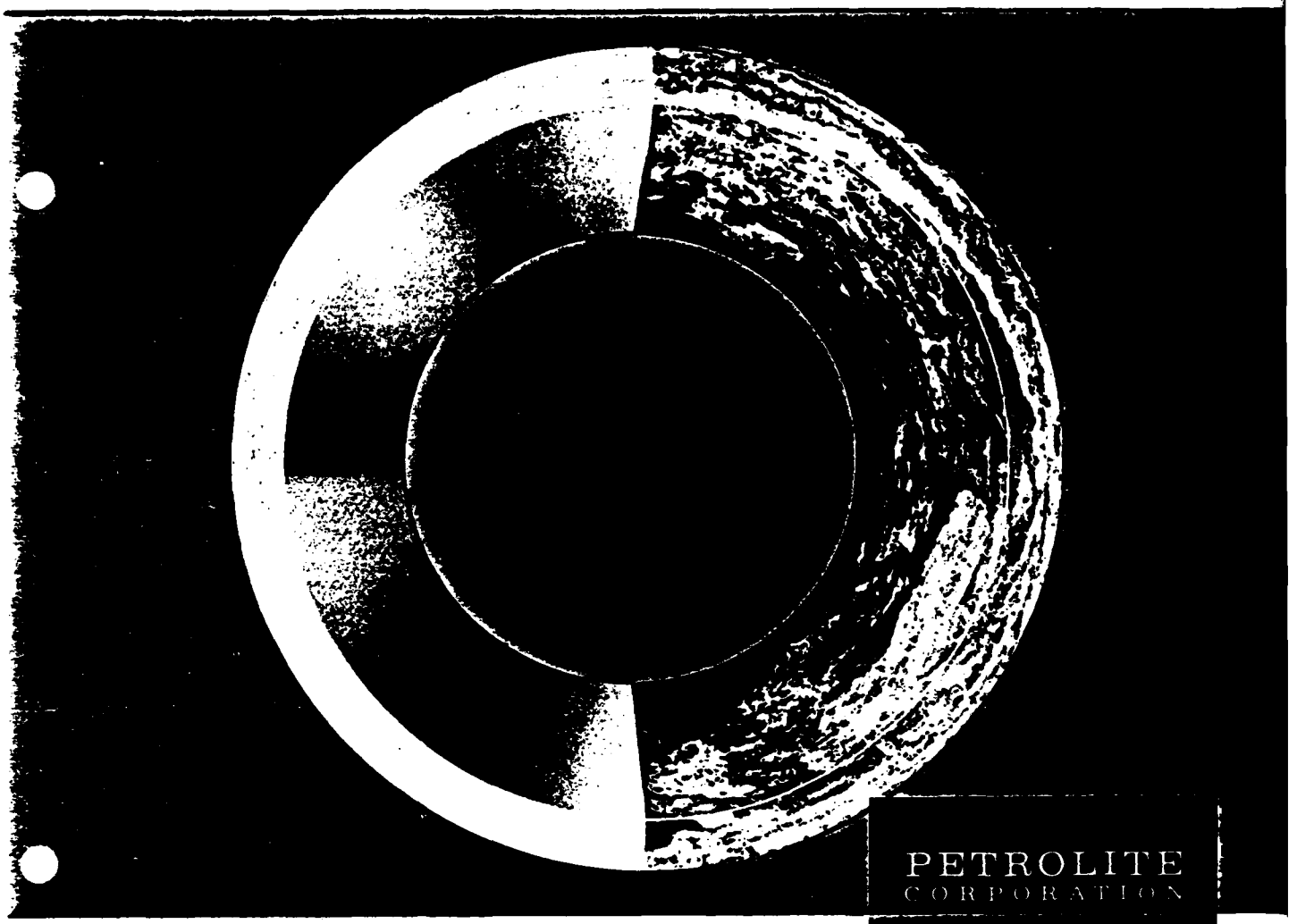
Shipping:

X-CIDE-401 is shipped in 55 gallon steel drums, F.O.B. St. Louis, Missouri.

Handling:

X-CIDE-401 is an industrial chemical and all the normal precautions used in handling industrial chemicals should be observed. See Label for First Aid Instructions.

EPA Registration No. 5009-14



PETROLITE
CORPORATION

TRETOLITE
DIVISION
Saint Louis, Missouri 63119

TOLAD. 245 *rust inhibitor*

PROTECT
Your Equipment...Your Products...Your Profit
with TOLAD 245

GENERAL DESCRIPTION

TOLAD* 245 Rust Inhibitor is an ashless organic fuel additive, soluble in hydrocarbons but insoluble in water, designed for use in all refined petroleum products. The addition of this inhibitor to a finished product stream affords protection to pipelines, tanks, pumps, and other products-handling equipment. TOLAD 245 is compatible with the commonly-used anti-oxidants, dispersants, metal deactivators, and dyes.

WHAT IT DOES

TOLAD 245 has a strong affinity for metal surfaces, particularly in an oxidizing environment where oxygen and carbon dioxide influence corrosion. This condition normally exists in product pipelines and storage facilities. TOLAD 245 establishes a protective monomolecular film on the surface of all metal in contact with the product stream. Because TOLAD 245 is entirely hydrocarbon-soluble, it will not be lost to "water bottoms" at pumping stations. Therefore, *only one inhibitor injection point is necessary to protect an entire system from refiner to consumer.*

WHY IT WAS DEVELOPED

Organic rust inhibitors have been used for many years as the most economical, most efficient, and safest method for protecting fuels and fuel transportation equipment. Prior products were developed primarily to offer good rust protection. Current fuel quality requirements of cleanliness and high WSIM ratings have focused attention on side effects characteristic of rust inhibitors. TOLAD 245 was specifically formulated to meet the new high quality requirements in today's fuels without contributing to any of the undesirable side effects.

WHY IS IT NECESSARY?

Rust and corrosion are directly responsible for two major unfavorable effects in product lines—product contamination and reduced capacity. These difficulties represent the most costly effects of poor corrosion control in product lines.

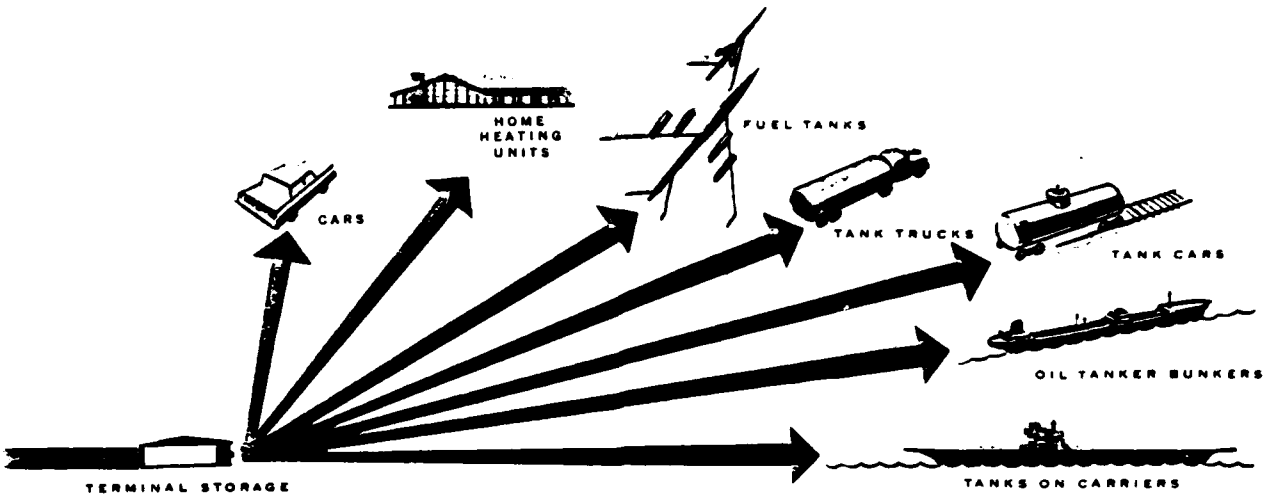
Products contaminated with rust particles must be settled, filtered, or processed in some manner before they pass market specifications. Also, rust particles erode pumps, valves, meters, and other equipment by impingement. In cases of severe corrosion, sections of the pipeline may have to be replaced.

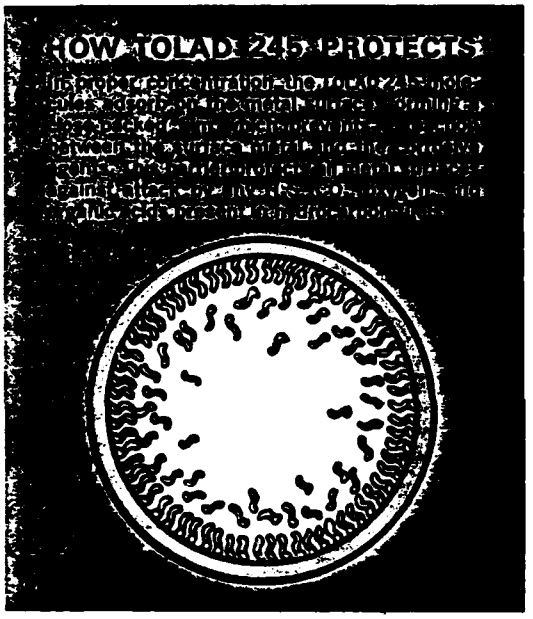
Reduced pumping throughput (low "C" factor) caused by line friction increases the cost of line operation. When this condition exists, the cost per barrel of products transported is higher, since the cost of transportation is divided among fewer barrels shipped.

TOLAD 245 OFFERS THESE BASIC ADVANTAGES...

1. Prevents product contamination caused by corrosion.
   Non-emulsifying formulation with excellent WSIM rating.
3. Reduces maintenance by keeping the line clean, eliminating frequent scraping.
4. Maximum throughput, high "C" factor.
5. Extends life of auxiliary equipment (meters, valves, screens, pumps, filters, etc.).
6. Approved under Military Specification MIL-I-25017 for use in military JP-4 fuel.
7. Completely soluble in all hydrocarbons.
8. The protective film formed by TOLAD 245 offers beneficial lubricity properties in fuel control valves and fuel metering systems.
9. Excellent low-temperature handling characteristics (−45° F pour point).

*Registered Trademark, Petrolite Corporation





HOW MUCH IS REQUIRED?

For maximum corrosion protection and minimum product contamination, a slight variance in initial treatment is recommended, depending on the condition of the pipeline.

New or clean lines

In new or clean lines, it is suggested that an initial injection of one gallon of TOLAD 245 be made for each thousand barrels of throughput. This concentration is maintained for one week in order to establish quickly a uniform protective film on all internal metal surfaces.

Moderately clean lines

When treatment is started in older lines where moderately high "C" factors are observed, a scraper program is usually initiated along with inhibitor injection. The normal procedure is to run scrapers daily (or as often as possible) and to inject TOLAD 245 at the rate of one gallon per thousand barrels of product pumped. This concentration is maintained until the fuel in the vicinity of the scraper comes through relatively clean. It is necessary to maintain high inhibitor concentrations during this time because most of the inhibitor will be adsorbed on the corrosion products (scale) and will not be available for adsorption on the clean areas in the pi[illegible]

Dirty lines

Where extremely dirty pipelines are to be treated, it is suggested that TOLAD 245 be started at a low rate and increased gradually as the scraper program progresses. This is necessary since TOLAD 245 is an excellent detergent and extremely rapid removal of dirt may cause scrapers to stick. Therefore, the usual procedure is to run a number of scrapers as often as possible prior to TOLAD 245 injection. The inhibitor is then injected at the rate of one quart per thousand barrels of products pumped, and in conjunction with a concentrated scraper program.

As the appearance of the hydrocarbon in the vicinity of the scraper indicates maximum cleanliness, the inhibitor rate is increased. The rate of injection is raised in one-quart increments until the gallon-per-thousand rate is reached. This rate is maximum, and is held until the line is considered to be clean.

Continuing protection

After initial treatment, the concentration of TOLAD 245 should be lowered. Minimum inhibitor concentration should be determined as described in "Evaluation of Treatment." *Usually one quart of TOLAD 245 per thousand barrels will maintain protection.*

EVALUATION OF TREATMENT

1. Samples of inhibited fuels may be sent to Tretolite's laboratory to determine the degree of protection in dynamic rust tests. Test methods are available which correlate with actual field experience. In addition, portable testing equipment can be scheduled to monitor entire pipeline systems.

2. Removable metal coupons or probes may be used to measure rust protection.

3. The degree of product contamination and frequency of filter change can be observed before and after treatment with TOLAD 245.

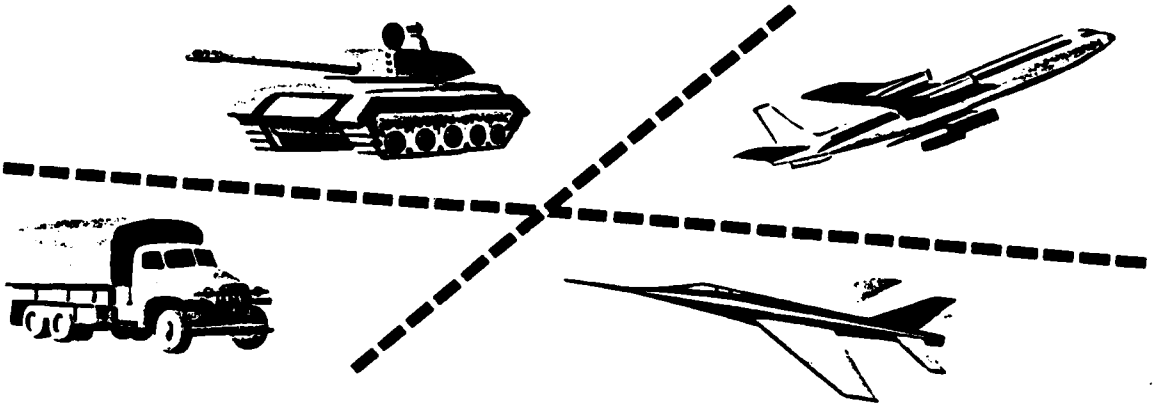
4. "C" factor (Hazen-Williams Coefficient) can be determined as a measure of performance.

Water separometer test is used for evaluating water-separating properties of fuels.

Spindle test determines effectiveness of rust inhibitor.

TYPICAL PHYSICAL PROPERTIES

Weight	**8.1 lb./gal.**
Flash Point (TOC)	**Above 130° F**
Pour Point	**—45° F**
Ash Content	**Nil**
Solubility in Hydrocarbon	**Soluble**
Solubility in Water	**Insoluble**



TRETOLITE DIVISION

369 Marshall Avenue, St. Louis, Missouri 63119

Offices and representatives in Al-Khobar, Bangkok, Barrel, Calgary, Frankfurt, Goteborg, The Hague, Istanbul, Kuwait, London, Maracaibo, Mexico City, Paris, Port of Spain, Rome, Singapore, Tehran, Tehran, Tokyo, Tripoli

977-AC-3R

Printed in U.S.A.

PETROLITE CORPORATION

TRETOLITE DIVISION
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(314) 961-3500 / TWX 910-760-1660 / Telex 44-2417

TOLAD T-245 Rust Inhibitor

WHAT IS IT?

TOLAD T-245 is a fuel soluble, ashless, organic rust inhibitor designed for use in all finished petroleum products to protect pipelines, tanks, pumps and vehicles from corrosion. TOLAD T-245 is compatible with other commonly used fuel additives.

HOW IT WORKS

TOLAD T-245 forms a thin tenacious film on metallic surfaces that isolates the metal from corrosion elements. This film also acts as a lubricant to reduce wear in areas such as aircraft fuel control systems and service station blending pumps.

WHY WAS IT DEVELOPED?

Obtaining good rust protection is not difficult. Obtaining good rust protection without effecting emulsion forming tendencies, as measured by the Water Separometer Index Modified rating, is quite another matter. TOLAD T-245 is specifically designed to give rust protection AND maintain high WSIM ratings.

TOLAD T-245 gives these benefits

1. Rust protection throughout an entire fuel distribution system - with only one injection point needed.
2. Little or no decrease in the WSIM ratings of fuels at normal treating ratios.
3. Excellent low temperature handling characteristics.
4. Completely soluble in JP-4 fuel and iso-octane - try this simple test with the additive you are using.
5. Prevents product contamination and filter plugging by preventing rouge type rust formation.

HOW MUCH IS REQUIRED?

This will vary with application. For general pipeline protection, a continuous injection of about 2 LB./1000 BBL. is a good starting point. Actual minimum injection rates are best established by corrosion coupon and/or electric resistant probe surveys in the field.

MILITARY APPROVAL

TOLAD T-245 is qualified under Specification MIL-I-25017 for use in fuel MIL-T-5624 (JP-4 and JP-5). This approval was granted on March 1, 1968.

TYPICAL PHYSICAL PROPERTIES

Flash Point, PMCC, °F.	90
Pour Point, ASTM D-97, °F.	below -40
Viscosity, SUS, @ 0°F.	1,000
@ 30°F.	280
@ 60°F.	110
@ 100°F.	58
Ash Content, % Maximum	.04
Solubility In Hydrocarbon	Soluble
Solubility In Water	Insoluble

HANDLING

TOLAD T-245 is an industrial chemical and should be handled with the same precautions as used with other petroleum products. Avoid open flame. Avoid skin and eye contact.

AVAILABILITY

TOLAD T-245 is supplied in 55-gallon nonreturnable steel drums and tank truck bulk quantities.

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TOLAD T-500 FUEL EMULSION PREVENTIVE

TOLAD T-500 is a liquid organic fuel soluble additive used to prevent emulsion and haze formation in gasoline, fuel oil and other refined products.

HOW IT WORKS

TOLAD T-500 prevents fuel haze by coalescing water droplets as they form and it acts as a surface active demulsifier to prevent fuel and tank bottom emulsions.

WHY WAS IT DEVELOPED

TOLAD T-500 was developed because of the problem of hazy fuels and storage tank emulsions caused by the increasing use of detergent and dispersant additives and by the temperature differentials encountered in pipeline transportation.

APPLICATION

TOLAD T-500 is recommended at concentrations ranging from 5 to 50 ppm depending upon the factors causing haze and emulsion formation. It should be used as a preventive treatment and therefore added to fuel before haze develops.

TYPICAL PHYSICAL PROPERTIES

Density @ 60°F., Lb./Gal.	8.1
Flash Point, °F., SFCC ASTM D-3243	112
Pour Point, °F., ASTM D-97	Below -30
Viscosity @ 0°F., SUS ASTM D-445	312
Viscosity @ 30°F., SUS ASTM D-445	128
Viscosity @ 60°F., SUS ASTM D-445	67

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"TOLAD" MULTIFUNCTIONAL GASOLINE ADDITIVE MFA-21

WHAT IS IT

TOLAD MFA-21 is a fuel soluble ashless, organic gasoline additive. It was designed to provide carburetor detergency, anti-icing and corrosion protection without causing haze, dirt or sludge suspension in fuel. TOLAD MFA-21 is compatible with other commonly used fuel additives.

HOW IT WORKS

TOLAD MFA-21 removes existing carburetor deposits and prevents further deposition by a strong detergent effect. The formation of an adherent additive film on carburetor surfaces repels water droplets and avoids the problem caused by ice crystal formation. This same additive film protects the entire fuel distribution system from corrosion, thus reducing contamination from particulate matter.

WHY WAS IT DEVELOPED

There has been industry interest to provide additional detergency to fuels by increasing the concentration of multipurpose additives. The detergent effects of these additives often caused problems of emulsion and haze in storage. TOLAD MFA-21 was developed to provide additional detergency at concentrations of 100 ppm or higher without causing emulsions, haze, or dirt suspension when gasoline contacts water in transport and storage.

HOW MUCH IS REQUIRED

TOLAD MFA-21 can be added to finished gasoline from 10 - 60 pounds per thousand barrels depending upon the degree of performance desired.

TYPICAL PHYSICAL PROPERTIES

WEIGHT	8.0 LB./GAL.
POUR POINT	Below -10°F.
FLASH POINT	Above 110°F.
ASH	NIL
PHOSPHORUS	NIL

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TOLAD 311

ANTI-STATIC ADDITIVE

GENERAL DESCRIPTION

TOLAD 311 is a non-metallic additive developed to improve the electrical conductivity of middle distillate fuels. By increasing a fuel's conductivity, the electrical charges generated during mixing and shipment are allowed to dissipate and thereby reduce the hazards of charge accumulation.

RECOMMENDED USAGE

It is recommended that the treated fuel have a minimum conductivity value of 50 CU* (generally accepted as a minimum safe value) at fuel use temperature. The concentration of TOLAD 311 required to provide this is 0.5 to 5.0 lbs./M bbl. in most distillate fuels. TOLAD 311 may be added as a concentrate or diluted with most hydrocarbons, if desired.

BACKGROUND

Hydrocarbon fuels can generate an electrostatic charge during handling and filtration. Since most fuels have rather low natural conductivities, the charges generated can accumulate with a resultant increase in field strength. If a spark discharge occurs in a combustible mixture, an explosion or fire may result. TOLAD 311 imparts increased conductivity to the fuel allowing the charges generated to dissipate quickly and reduce their potentially dangerous accumulation. The use of TOLAD 311 does not obviate the need to follow accepted safety practices such as proper grounding and flow control during fuel handling and loading.

HANDLING

The toxicological properties have not been fully evaluated and proper precautions, common to many hydrocarbons, should be taken in handling. Prolonged or repeated skin contact should be avoided as skin irritation may occur. In case of skin contact, flush thoroughly with water and wash with soap and water.

TYPICAL PHYSICAL PROPERTIES

Weight	7.4 LB./GAL.
Flash Point (PMCC)	105°F.
Pour Point (ASTM D-97)	0°F, Maximum
Viscosity @ 32°F.	7490 SUS
" @ 60°F.	1310 SUS
" @ 100°F.	239 SUS
.sh, wt. %	0.00

* CU 1 Conductivity Unit = 1 Picosiemen/meter = 1 Picomho/meter

PETROLITE CORPORATION

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INDUSTRIAL PRODUCTS PRICE LIST
EFFECTIVE APRIL 15, 1980

Compound	Price	FOB(1)	Compound	Price	FOB (1)	Compound	Price	FOB (1)
A-3089	$ 6.65	B/C/S	D-80	$ 8.50	B/C/S	DS-638	$ 6.65	B/C/S
ACW-11	10.15	B/C/S	D-83	9.85	B/C/S	DS-651	6.90	B/C/S
ACW-15	8.50	B/C/S	D-84	5.75	B/C/S	DS-655	6.80	B/C/S
ACW-17	9.80	B/C/S	D-89	12.90	B/C/S	DS-656	6.35	B/C/S
ACW-18	9.30	B/C/S	D-90	2.40/#	B/C/S	DS-659	7.00	B/C/S
ACW-20	11.45	B/C/S	D-91	7.30	B/C/S	DS-660	7.00	B/C/S
ACW-32	5.75	B/C/S	D-95	10.50	B/C/S	DS-677	6.50	B/C/S
ACW-33	3.25	B/C/S	D-97	10.15	B/C/S	DS-689	6.65	B/C/S
ACW-34	9.10	B/C/S	D-98	4.60	B/C/S	DS-690	6.65	B/C,
ACW-57	13.50	B/C/S	D-102	4.20	B/C/S	DS-4036	5.50	B/C/S
AF-16	8.25	B/C/S	D-109	4.25	B/C/S	DS-4055	5.90	B/C/S
AF-17	11.75	B/C/S	D-500	4.85	B/C/S	DS-4056	5.50	B/C/S
AF-21	8.60	B/C/S	D-501	6.75	B/C/S	H-0307	.87/#	B/C/S
AF-33	9.35	S	D-503	20.90	B/C/S	ICA-1	4.35	B/C/S
AF-35	8.40	B/C/S	D-504	10.50	B/C/S	ICA-2	5.25	B/C/S
AF-37	7.45	B/C/S	D-1982	6.00	B/C/S	IND-1	1.15/#	B/C/S
AF-42	11.85	B/C/S	DP-9103	8.40	B	IND-2	1.60/#	B/C/S
AF-44	6.15	B/C/S	DP-9107	7.15	B	IN-4D	4.65	B/C/S
AP-5518	6.95	B/C/S	DS-415	6.50	B/C/S	IN-5D	5.85	B/C/S
AW-5533	7.10	B/C/S	DS-424	6.50	B/C/S	K-77W	7.70	S
D-3	4.95	B/C/S	DS-629	6.70	B/C/S	K-157	5.50	B/C/S
D-13	6.25	B/C/S	DS-636	6.65	B/C/S	K-157C	8.55	B/C/S

Compound	Price	FOB (1)
190	$ 5.25	B
K-407	12.45	B/C/S
K-424	6.90	B/C/S
K-430	9.80	B/C/S
K-430W	8.40	B/C/S
K-437	7.10	B/C/S
K-443	8.65	B/S
K-445	7.50	B/C/S
K-447	10.75	B/S
K-449	8.25	B/C/S
K-450D	8.35	B/C/S
KG-1004	6.00	B/C/S
KG-1009	10.15	B/C/S
KI-16	6.70	S
KI-18	10.00	S
KI-30	7.65	B/C/S
KI-34	10.20	B/C/S
KI-39	11.10	S
KI-46	5.85	B/C/S
KI-50	13.00	S
KI-51	4.25	B/C/S
KI-52	10.10	B/C/S
KI-55	19.00	S
KI-58	10.20	S
KI-59	12.85	S
KI-61	$ 5.25	B/C/S
KI-62	10.60	B/C/S
KI-63	4.70	B/C/S
KI-66	12.70	S
KI-77D	31.20	S
KI-78	7.50	B/C/S
KI-80	9.90	B/C/S
KI-81	7.75	C
KI-86	9.75	B/C/S
KI-160	10.40	S
MFA-2 I	10.95	C/S
PA-602	6.75	B/S
RH-1067	6.15	B/C/S
RI-1	10.00	B/C/S
RI-3	5.85	B/C/S
RI-13	6.25	B/C/S
RI-25	6.35	B/C/S
RI-28	6.00	B/C/S
RI-29	6.90	B/C/S
RI-35	6.95	B/C/S
RI-38	6.25	B/C/S
RI-43	6.75	B/C/S
RI-47	6.45	B/C/S
RI-48	6.35	B/C/S
RI-51	6.00	B/C/S
RI-53	$ 7.10	B/C/S
RI-56	6.80	B/C/S
RI-57	7.20	B/C/S
RI-60	7.40	B/C/S
RI-64	8.00	B/C/S
RI-66	6.50	B/C/S
RI-827	7.10	B/C/S
RP-805	7.00	B
RP-841	7.35	B
RP-849	7.25	B
RP-889	6.50	-
RP-2207	7.25	B/C/S
RP-2328	6.30	B/C/S
RP-2334	6.90	B/C/S
RW-9537	6.90	B
RY-9539	6.90	B
T-31	6.95	S
T-35	6.50	S
T-36	5.00	S
T-37	4.00	S
T-61	5.10	C
T-61P	.72/#	C
T-105D	13.20	C/S
T-199D	8.15	C/S
T-244	6.25	C/S

Compound	Price	FOB (1)	Compound	Price	FOB (1)	Compound	Price	FOB (1)
T-245	$ 6.25	C/S	TB-20	$ 6.60	B/C/S	TFL-399D	$ 6.20	B/C/S
T-249D	5.75	C/S	TB-27	6.35	B/C/S	TFL-402	6.20	B/C/S
T-260	10.00	C/S	TCW-10	8.30	B/C/S	TFL-404	6.30	B/C/S
T-264	7.75	C/S	TCW-11	8.30	B/C/S	TFL-405	6.80	B/C/S
T-284	7.25	C/S	TCW-12	8.30	B/C/S	TI-8	9.00	B/C/S
T-285	9.40	C/S	FR-501	7.00	B/C/S	TI-9	5.70	B/C/S
T-286	8.80	C/S	TFL-300	5.70	B/C/S	TK-14	4.70	B/C/S
T-292	7.70	C/S	TFL-313	4.05	B/C/S	TK-16	3.25	B/C/S
T-303	6.60	C/S	TFL-326	7.90	B/C/S	TK-29	5.10	B/C/S
T-304	9.45	C/S	TFL-330	6.55	B/C/S	TK-502	4.70	B/C/S
T-311	7.70	C/S	TFL-331	8.85	B/C/S	TSP-100	8.05	B/C/S
T-316	4.85	C/S	TFL-333	9.50	B/C/S	TSP-105	9.55	B/C/S
T-327	10.25	C/S	TFL-335	5.50	B/C/S	TSP-107	7.00	B/C/S
T-331	10.25	C/S	TFL-362	8.40	B/C/S	TSP-110	6.00	B/C/S
T-346	6.70	S	TFL-365	7.35	B/C/S	TSP-120	10.00	B/C/S
T-347	6.10	C/S	TFL-366	8.65	B/C/S	TSP-133	5.45	B/C/S
T-357	13.50	S	TFL-370	7.15	B/C/S	TSP-136	75.00/50#	B/C/S
T-358	10.25	C/S	TFL-381	9.00	B/C/S	TSP-143	7.75	B/C/S
T-360	7.00	C/S	TFL-383	7.35	B/C/S	TSP-145	5.95	B/C/S
T-362	8.35	C/S	TFL-386	7.85	B/C/S	TSP-146	5.75	B/C/S
T-405D	12.65	C/S	TFL-389	5.30	B/C/S	TSP-152	6.00	B/C/S
T-406	12.75	C/S	TFL-391	6.65	B/C/S	TSP-156	12.15	B/C/S
T-500	5.60	C/S	TFL-397	7.15	B/C/S	TSP-157	6.50	B/C/S
T-507	8.15	C/S	TFL-398*	6.20	S	TSP-159	8.50	B/C/S

Compound	Price	FOB (1)	Compound	Price	FOB (1)	Compound	Price	FOB (1)
'-160	$ 7.70	B/C/S						
TSP-161	7.20	B/C/S						
XC-102	11.00	B/C/S						
XC-236	22.40	B/C/S						
XC-320	9.60	B/C/S						
XC-370	9.35	B/C/S						
XC-401	14.05	B/C/S						
XC-402	10.50	B/C/S						
XC-505	8.00	B/C/S						
XC-507	11.80	B/C/S						
XC-508	35.25	B/C/S						
XC-510	15.60	B/C/S						
XC-511	13.95	B/C/S						
X-1395	10.90	B/C/S						

*TFL-398 Bulk Only
FOB Laurel, Ms. $5.65 Gallon

Terms: Net 30 Days

(1) FOB Point B=Brea, CA
C=Bayport, Tx.
S=St. Louis, Mo.

All prices quoted are per gallon except where otherwise indicated.

PRICES SUBJECT TO CHANGE
W IOUT NOTICE.

INDUSTRIAL DRY PRODUCT PRICE LIST

(F.O.B., ST. LOUIS, MO.)

Product	Quantity Per Package	1-9	10-19	20-39	40-119	120 & Up
TFL-351	50#/bag	$4.00/#	$3.75/#	$3.40/#	$2.95/#	$2.90/#
TFL-352	50#/bag	$3.10/#	$2.75/#	$2.50/#	$2.30/#	$2.20/#
TFL-353	50#/bag	$4.00/#	$3.75/#	$3.55/#	$3.25/#	$3.15/#
TFL-358	50#/bag	$4.45/#	$4.20/#	$3.85/#	$3.40/#	$3.25/#

PRICES SUBJECT TO CHANGE WITHOUT NOTICE

Effective April 15, 1980

DISCOUNT SCHEDULE

PURCHASED IN DRUMS:

To determine the F.O.B. cost per drum:

1. Determine base price per gallon of formula.
2. Multiply by 55 to obtain drum price.
3. Determine total number of drums purchased.
4. Subtract quantity discounts using one of the tables shown below:

		DISCOUNT PER DRUM					
	BASE PRICE	1-9 dr.	10-39 dr.	40-74 dr.	75-149 dr.	150-224 dr.	225 drums
Without blanket order	$5.00 and up	0	$5	$6	$8	$9	$10
	Below $5.00	0	$3	$4	$5	$5	$ 5

		100 dr. B/O	150 dr. B/O	225 dr. B/O
With blanket order	$5.00 and up	$8	$9	$10
	Below $5.00	$5	$5	$ 5

PURCHASED IN BULK:

To determine F.O.B. Bulk Price per Gallon:

1. Determine base price per gallon of formula.
2. Determine total number of gallons purchased.
3. Subtract quantity bulk discount using one of the tables shown below:

		DISCOUNT PER GALLON			
	BASE PRICE	2200-4124 gal.	4125-8249 gal.	8250-12,374 gal.	12,375 gal. & up
Without blanket order	$5.00 and up	23¢	26¢	28¢	30¢
	Below $5.00	19¢	21¢	21¢	21¢
		550 gallons and up			

		100 dr. B/O	8250 gal. 150 dr. B/O	12,375 gal. 225 dr. B/O
With blanket order	$5.00 and up	26¢	28¢	30¢
	Below $5.00	21¢	21¢	21¢

ANNUAL BLANKET ORDERS

Tretolite Division offers the following Blanket Order Plan in addition to its regularly quoted quantity discounts.

1. The customer issues to Tretolite a blanket purchase order for liquid products to be delivered within 12 months. The minimum blanket order is for 100 drums of 5,500 gallons. Blanket orders can also be written for 150 drums and 225 drums to qualify for a larger discount.

2. Our products will be delivered to you when and as you need them within a 12 month period.

3. The customer will be invoiced on each delivery and will receive the quantity discount applicable to the blanket order.

4. If the customer does not purchase his blanket order requirement of Tretolite's products during the designated 12 month period he will be invoiced for actual shipments in accordance with Tretolite's price and discount schedule in effect at the time of shipment.

The following statement must be shown on Blanket Purchase Orders:

"This purchase order is for a minimum of (100, 150, 225)* drums of Tretolite Division's liquid products purchased within 12 months of purchase order date. It does not cover less than 55 gallon drum quantities. Solid products do not qualify for blanket orders".

"All invoices covered by this blanket order will be at the discount applicable to the blanket order. If, during the designated 12 month period, less than the specified number of drums of Tretolite Division's products are purchased. Tretolite will invoice for actual shipments in accordance with their price and discount schedule in effect at time of shipment".

Tretolite's warehouses are located in the major oil producing areas to provide you with readily available products, eliminating the need for large customer inventories.

*Indicate number of drums.

CREDITS AND RETURNS

Tretolite Division will not accept for credit or exchange products older than one year. Products less than one year old may be returned to a Tretolite location if approved by the District Manager.

A 20% restocking charge will be made for chemical returned to stock location or warehouse for customer convenience. The freight is to be prepaid by customer.

The purchase order number or date of purchase of the returned chemical is necessary to support the credit memo and should be put on the Bill of Lading when possible.

PALLETIZED SHIPMENTS

A charge of $16.00 per pallet (3 drums or less) will be added for palletizing drums.

5 - GALLON CONTAINERS
LIQUID PRODUCTS

Pricing of liquid products add $1.65 per gallon to the alphabetical list base price. Five gallon container purchases are not eligible for discounts.

Prices for quantities in excess of those stated herein will be quoted on request.

APPENDIX A

PART 4

UOP Corporation

technical bulletin

POLYFLO® 130

ANTI-FOULING AND STABILIZING AGENT FOR DISTILLATE FUELS

POLYFLO 130 is a corrosion inhibiting, polymeric type, multi-purpose fuel oil additive. Its primary functions are those of an anti-fouling agent for heat exchangers and a thermal stabilizer for residual oils. It serves as a detergent for storage tank sludge, as a dispersant for wax and sludge deposits, and as a pour point depressant for many blended distillate oils.

POLYFLO 130 was developed as an alternative to POLYFLO 100, for use under cold weather conditions. In a number of cases, it is a better fuel oil stabilizer, though its action is apt to be specific, depending upon the oil to be treated. And in an even greater number of cases, it is superior to all members of the POLYFLO family in its ability to inhibit rust formation.

TYPICAL PHYSICAL PROPERTIES

Physical Form	Liquid
Gravity at 60°F	24.0° API
Density, g. ml at 15°C	0.9095
Weight, at 60°F	7.6 lbs gal
Pour Point	-5°F (-21 C)
Cloud Point	2°F (-17° C)
Flash Point, Tag Open Cup	122°F (50°C)
Flash Point, Pensky-Martens	104°F (40°C)
Viscosities	
Kinematic at 60°F (15.5°C)	196 cs
Kinematic at 100°F (38°C)	86 cs
Universal at 100°F	398 sec
Universal at 60°F	905 sec
Universal at 40° F	1674 sec
Universal at 20 F	3237 sec
Universal at 6.3° F (-14° C)	5000 sec

DOSAGE

Normal dosage levels vary from about 5 to 50 parts per million (0.0005% to 0.005%, by weight, or 2 to 15 lbs 1000 bbls).

Each of the POLYFLO compounds exhibits different degrees of effectiveness in different stocks, so that it is difficult to recommend one over the other without adequate test data. Indeed, in solving some complex problems, blends of additives are sometimes recommended.

EVALUATION OF PROTECTIVE ACTION

Until recently, a wide gap existed between the storage stability of cracked blends and straight-run oils. Cracked components tended (and still do) to form soluble gums and insoluble sediments. Additional refinery treatment, including hydrogenation, has narrowed the gap. But with each processing treatment adding to the costs, e.g. in excess of 10c/bbl for minimum acceptable results from hydrogenation, the addition of inhibitor-dispersants to chemically treated oils offers distinct economic advantages.

UOP Process Division
Universal Oil Products Company
20 UOP Plaza – Algonquin & Mt Prospect Roads
Des Plaines, Illinois 60016 312-391-2000

technical bulletin

POLYFLO® 130

Extensive research by UOP in the inhibitor field led to the development of the POLYFLO series of additives for handling the problems of gum and sediment formation, filterability, color development, water hold-up, corrosion, and pumpability. These POLYFLO additives differ from one another in their ability to provide answers to problems encountered with different oil blends under a variety of conditions. To choose the correct POLYFLO for protection of a particular oil, under a given set of conditions, Universal employs a series of evaluation tests that have proven practical.

In running these tests in the laboratory, we first obtains preliminary information by a microscopic, physical and chemical examination of the oil for known deleterious compounds such as copper, thiophenols and nitrogen. Samples of the oil to be protected are then run through screening tests to determine the most promising additive and concentration. These include one and two day accelerated heat tests for evaluation of color changes and sediment formation. The selected additives may then be subjected to larger scale storage tests at 110°F for periods of up to 3-4 months, during which relative sedimentation, filterability and color development are periodically checked. Naturally, such factors as caustic scrubbing and blend ratios of various distillates may also be considered in the program.

The result of such testing often shows that an additive which may be competitive with a specific POLYFLO under one set of test conditions is non-competitive in other tests. UOP's recommendations are therefore based on over-all performance data rather than on the results of one specific test.

APPLICATION EXAMPLES

The thermal stabilizing values of POLYFLO 130 as a fuel oil additive are indicated by the data in Table I. Preliminary data of the type shown are the results of accelerated heating tests. In this particular case, the tests were run on a heating oil blend of 50% light cycle oil and 50% straight run fuel oil having an original ASTM Color of 1½ and Photo Color of 98.3.

Table I

One Day Fuel Oil Stability Test

UOP Method No. 413-61*

Additive	Concn ppm	ASTM Color	Photo Color	Sediment mg. L
Blank	0	3	46.0	22
POLYFLO 130	40	1½	70.5	2
PRODUCT "T"	40	2	63.5	⅛
PRODUCT "U"	40	1½	70.5	7

* 16 hours at 212°F in oxygen medium.

Another type of preliminary test occasionally used by Universal involves heating the oil in air for 48 hours at 212°F. The 50-50 blend used in the test in Table I showed the "Blank" dropping to an ASTM Color of greater than 8 (Photo Color of Zero), while the blend containing 40 ppm POLYFLO 130 showed an ASTM Color of 2¼. The blend with 80 ppm of POLYFLO 130 gave an ASTM Color of 2 after 48 hours, while competitive Products "T" and "U" gave values of 4 and 3 respectively.

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Des Plaines, Illinois 60016 312•763-6000

Similar, accelerated tests on blends containing different ratios of the same light cycle oil and straight-run oil showed that POLYFLO 130 maintained its superiority over the same competitive products, particularly with respect to low sediment formation.

Storage tests of several months duration are frequently run at 110°F on blends containing the most promising of the additives or addition combinations. In many cases, POLYFLO 130 confirms its margin of superiority; in other cases, another of the POLYFLO series of compounds is apt to be the preferred additive.

The Santa Fe Heating Test (90 minutes at 300°F, after 12 weeks storage at 110°F) may also be employed by UOP for screening purposes. In many cases, oils to which POLYFLO 130 has been added react favorably; in other cases, the use of POLYFLO 120 or 121 (inhibitor types) may be indicated.

To evaluate the anti-screening-clogging characteristics of oils UOP used Socony Mobil Tentative Method No. 530-58. In this method, the oil is circulated repeatedly through a filter so that the sediment build-up over a period of time can be measured. Thus the dispersing action of the additive can be evaluated, for it seems obvious that an additive which permits agglomeration of suspended particles will result in a poor rating. The rating is shown as the per cent reduction in the weight of the screen deposit, and a fuel with a rating above 90% is considered excellent.

Table II

Anti-Screening-Clogging Characteristics of No. 2 Fuel Oil

Oil Used: No. 2 Heating Oil; S-88-62, UOP No. 42-2054

Additive	ppm	% Rating
POLYFLO 130	16	95
POLYFLO 130	33	95
POLYFLO 130	58	97
POLYFLO 100	33	94
Product "P"	16	12
Product "P"	33	36
Product "P"	117	48

Competitive Product "P" was included in this Table because it had been found to be competitive with POLYFLO 130 in the heating and storage stability tests of this particular oil. But the Socony Mobil Test shows it to be definitely inferior as a detergent-dispersant.

POLYFLO 130 shows its rust inhibiting values in ASTM Turbine Oil Corrosion Test D 667, which use modified resistance probes, synthetic sea water and a temperature of 140°F.

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technical bulletin

POLYFLO 130

Table III
Turbine Oil Corrosion Test
Oil Used: No. 2 Fuel Oil (UOP Method 354-58)

Additive	ppm	Mils per year
Blank	0	114
Blank	0	124
POLYFLO 130	5	99
POLYFLO 130	10	54
POLYFLO 130	20	25
POLYFLO 130	40	15

The difference between oils also shows up on these corrosion tests. For example, a blend of 30% light cycle oil (caustic washed) and 70% light gas oil which gave corrosion values ranging from 105 to 141 mpy for 4 blanks, showed values of 1 and less than 1 mpy for the sample containing 40 ppm and 80 ppm of POLYFLO 130. It is also worthy of note that this same 30-70 blend, when subjected to the one day fuel oil stability test, gave an ASTM Color of 3 and 11 mg/Liter sediment. When protected by 40 ppm POLYFLO 130, an ASTM Color of $2^1/_2$ and a sediment of only 1 mg/Liter was obtained. Results such as these not only show the value of running several tests but also prove that POLYFLO 130 exhibits corrosion inhibition values in addition to its previously demonstrated dispersant and detergent properties.

POLYFLO 130 also serves as a pour point depressant for a number of blended distillate oils, although its effect is not generally predictable. Reductions of 15-30° F for 40-50° F pour point oils have been noted.

HANDLING

POLYFLO 130 is preferably added to fuel oils by continuous injection into a flowing stream. Its handling presents no unusual hazard, but normal precautions for handling petroleum additives should be taken. Adequate protective clothing and proper ventilation is recommended; in event of skin contact, wash off promptly with soap and water.

SHIPPING INFORMATION

Bill of Lading Description: "Fuel Oil Treating Compound" for preventing Precipitation of sediment.

Containers: Non-returnable steel drums
400 pounds net, 450 pounds gross weight

Warehouses:

Houston, Texas
Tulsa, Oklahoma
Mt. Vernon, Wash.
Long Beach, Calif.
McCook, Illinois
E. Rutherford, N. J.

March, 1967
T-391-B

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Universal Oil Products Company
20 UOP Plaza – Algonquin & Mt Prospect Roads
Des Plaines, Illinois 60016 312-763-6000

TECHNICAL BULLETIN

POLYFLO® 100

DISPERSANT – STABILIZER FOR DISTILLATE AND RESIDUAL FUELS

POLYFLO 100 is an ashless, oil-soluble, multi-purpose dispersant-stabilizer, designed to improve and protect distillate fuels. It is a polymeric type additive that fulfills a number of functions:

1. Improves finished products
   a) As a dispersant-stabilizer for No. 2 fuel oils
   b) As a dispersant in residual oils
   c) As a pour point depressant for No. 2 fuel oils
2. Serves as a processing aid
   a) As an antifouling agent in crude exchangers
   b) As an antifouling agent in preheat exchangers for naphthas
   c) In alkylation units to neutralize and disperse decomposition products of acid esters

TYPICAL PHYSICAL PROPERTIES

Physical Form	Liquid
Gravity at 60°F	26.6° API
Density at 15°C	0.894 g/ml
Weight at 60°F	7.5 lbs/gal
Pour Point	60°F
Flash Point, Tag Open Cup	121°F (50°C)
Flash Point, Pensky-Martens	100°F (38°C)
Viscosities	
Kinematic at 38°C	15 cs
Universal at 100°F	78 sec
Universal at 62°F	273 sec

DOSAGE

Recommendations for the required concentration of POLYFLO 100 depend upon the application involved and the severity of the problem. Usage levels may vary from about 5 parts to 50 parts per million (0.0005% to 0.005% by weight, or 2 to 15 pounds per 1000 barrels).

Table 1

Suggested Dosage Levels

Application	lbs/MB	g/m^3
Antifouling agent for heat exchangers	1½-9	5-30
Thermal stabilizer for distillate and residual fuels	3-12	10-40
Dispersant-stabilizer for diesel and furnace oils	3-12	10-40
Pour point depressant for blended distillate oils	3-90	10-300

PROTECTING BLENDED FUELS

Demands for improved distillate fuel products and the concomitant increasing use of blends of straight-run and catalytically cracked products have emphasized the problems of products protection. Cracked components, in particular, are quite susceptible to oxidation and to chemical changes which result in the formation of gums and insoluble sludges. Selective hydrogenation of cracked stocks, as in Unifining, assists in removing contaminants and in saturation of olefinic hydrocarbons, but it is appreciably more expensive than the use of stabilizing additives. Consequently, the current trend is toward combinations of processing treatments and use of additives designed to meet individual fuel stability requirements on the most economical basis.*

In developing the POLYFLO family of compounds, it was known that no single additive could solve all the stabilization and dispersant needs of all types of fuels. Several different POLYFLO products were, therefore, synthesized to meet the various needs. POLYFLO 100 was designed to serve as a dispersant-stabilizer for distillate and residual fuel oils, as the following data indicate.

APPLICATION EXAMPLES

Antifouling Agent – to prevent deposition of gum and carbonaceous matter in heat exchangers. These may be heat exchangers through which pass process streams such as crude oil, distillation products, or the charge to a Platformer* or Unifiner*. For example, in one refinery, before the use of POLYFLO in a catalytic reformer operating on Pennsylvania naphtha, the exchanger fouled so badly in 6 to 8 weeks' operation that the pressure drop across it increased from 5 to 50 pounds, necessitating shut down of the unit. After addition of 10 parts per million of POLYFLO 100 to the reformer charge, the pressure only rose from 5 to 12 pounds in 3 months' operation. Visual inspection showed a substantial deposit in the heat exchanger when operating without POLYFLO 100, while inspection of the equipment after the dispersant had been used showed a marked decrease. For other examples, see Graph No. 1 and Tables 2 and 3. Graph No. 1 shows the value of POLYFLO 100 addition to a crude unit in another refinery plagued with the plugging of feed effluent heat exchangers. The POLYFLO injection was started midway through Run No. 1. It was continuously injected during Run No. 2. In both runs the crude charge was kept constant. The value of POLYFLO 100 is, and was, obvious.

In order to run comparative tests on a laboratory scale basis, UOP frequently runs the ASTM Fuel Coker tests to compare fuels with and without added POLYFLO 100. This ASTM Method D 1660-61T is used to measure the high temperature stability of a fuel. The fuel being evaluated is pumped at a specified rate (6 pounds per hour for 5 hours) through a simulated preheater section and thence through a heated filter section which represents a nozzle area or small fuel passages. A precision sintered stainless steel filter in the heated filter section traps fuel degradation products formed during the test. The extent of the build-up of these trapped particles is noted as an increased pressure drop across the test filter. This pressure differential, in combination with the deposit condition of the preheater, is used as an assessment of the thermal stability of the fuel.

As Table 2 below shows, the reformer feedstock was stable under the 300°F preheater and 400°F filter test conditions. However, the pressure drop across the filter increased to 25 inches of mercury in 285 minutes under higher preheater and filter temperature conditions. Table 3 shows the heavy naphtha plugged the filter even more quickly. In all cases, the runs were continued for the full 300 minutes in order to obtain the desired heater-tube ratings. These ratings, which indicate tube deposits along a 13 inch section of the preheater tube, are rated on the ASTM Color Standard (zero indicating no visible deposits). In the case of competitive Product "N", it is evident from Table 3 that it not only permits deposits in the first five inches of the preheater tube but also permits plugging up of the filter faster than the minimum test limit of 300 minutes.

*Trademark

Tables 2 and 3 both show that POLYFLO 100, though it may sometimes permit barely visible deposits at the 20 ppm level, can disperse fuel degradation products so well that little or no pressure differential across the filter exists throughout the standard 300 minute test period.

Table 2

CFR Coker Test

Samples: Reformer Feedstock
Test Conditions: 300°F Preheater and 400°F Filter Temperature, 6 pounds per hour fuel flow

	Filter Time, Min.	Δp, Hg"	Preheater Rating by inches to 13-inch length
As received	300	0.8	0, 0, 0, etc. to 13 inches
Test Conditions: 400°F Preheater and 500°F Filter Temperature, 6 pounds per hour fuel flow			
As received	285/300	25.0	0, 0, 0, etc. to 13 inches
POLYFLO 100, 10 ppm	300	0.1	1, 3, 3, 2, 1, 0, 0, etc. to 13 inches
POLYFLO 100, 20 ppm	300	0.0	0, 0, 2, 0, 0, etc. to 13 inches
Product "N," 20 ppm	124/300*	25.0	4, 4, 4, 4, 2, 2, 0, etc. to 13 inches

*The notation "124/300" means that the pressure of 25" of Hg was reached in only 124 minutes rather than the 300 minutes used for JP-4 stability. It also means the filter was by-passed and the run continued to 300 minutes in order to obtain heater-tube ratings.

Table 3

CFR Coker Test

Sample: Heavy Naphtha
Test Conditions: 400°F Preheater and 500°F Filter Temperature, 6 pounds per hour fuel flow

	Filter Time, Min.	Δp, Hg"	Preheater Rating by inches to 13-inch length
As received	70	25.0	0, 0, 0, 0, etc. to 13 inches
POLYFLO 100, 20 ppm	300	0.3	0, 0, 0, 0, etc. to 13 inches
Product "N," 20 ppm	220*	25.0	1, 2, 3, 2, 1, 0, etc. to 13 inches

*This run with a so-called competitive product stopped at 220 minutes. It was evident the tube rating would have been much worse had the run been continued and the filter by-passed.

Stabilizer-Dispersant: To reduce color formation and to prevent or decrease sediment and sludge formation in diesel and furnace oils during storage. The two tables that follow show the effect of POLYFLO 100 addition to a typical No. 2 fuel oil:

Table 4

One Day Fuel Oil Stability Test

UOP Method No. 413-61[a]

Additive	Concn. ppm	ASTM Color	Sediment mg/100 ml
None	0	2½	2.1
POLYFLO 100	40	1½	0.3
POLYFLO 100 CuDeact AW[R] (50)	40 2	1	0.1

(a) 16 hours at 212°F in oxygen medium

Table 5

Heating Oil Stability Tests[b]

Additive	ppm	Accelerated Test ASTM Color 24 hr.	Accelerated Test ASTM Color 48 hr.	Storage Test Sediment mg/100 ml
None	0	2½	3½	3.6
POLYFLO 100	20	1½	3	—
POLYFLO 100	40	1	2	[illegible]
POLYFLO 100	80	1	1½	0.9

(b) Accelerated test involves heating for 48 hours at 212°F. Storage test covers 90 days at 110°F.

Both tables show that addition of POLYFLO 100 to a typical heating oil greatly improves the oil's resistance to color degradation and formation of sediment. The addition of 2 ppm of UOP'S Copper Deactivator AW(50) to 40 ppm of POLYFLO 100 results in still further improvement — a synergistic effect.

When added to No. 2 fuel oils, POLYFLO at 20-40 ppm will enable most oils to pass the Socony Mobil Analytical Method for Dispersancy (Tentative Mobil Method 530-58) with a rating of 90% or better. This Method determines the anti-screen-clogging characteristics, the rating indicating the percent reduction in the weight of screen deposit. This shows that POLYFLO 100 has the ability to disperse solid particles in such a finely divided form that they will not clog the filter screens. Thus POLYFLO 100 serves both as an inhibitor and a dispersant.

Inhibitor-Dispersant: To prevent wax and sludge deposits in storage tanks holding crude oil or residual fuels (e.g., No. 5 and No. 6 fuel oils), and to peptize and disperse such deposits when they have already formed. As an inhibitor, it reduces and controls sludge formation in these high viscosity stored fuels. As a dispersant, it controls sludge particle size, prevents agglomeration and deposition. It also has been successfully used in eliminating existing deposits in such tanks when added to the fuel going in and out of the tank.

Pour Point Depressant: It is often an effective pour point improver for blended distillate oils, although its effect is not generally predictable. Reductions of 15-30°F for 40-50°F pour point oils have been noted. It will also improve the pumpability of distillate oils at low temperatures.

Table 6

POLYFLO 100
As a Pour Point Modifier

Sample Designation	No. 5 fuel oil
Sample Number	212
UOP Number	71-4898
Pour Points	
Original (no additive)	25°C (77°F)
Plus 50 ppm POLYFLO 100	-5°C (23°F)
Plus 150 ppm POLYFLO 100	-10°C (14°F)
Plus 300 ppm POLYFLO 100	-15°C (5°F)

HANDLING

POLYFLO 100 is preferably added to hydrocarbon products by continuous injection into a flowing stream. The injection system should be capable of accurate proportioning but need not be complex. Batch addition may also be practiced where the additive must be added to a product already in a tank. The addition should be gradual, and followed by thorough agitation of the oil by recirculation or mechanical mixing.

The handling of POLYFLO 100 presents no unusual hazard, but normal precautions for handling petroleum additives should be taken. Adequate protective clothing and proper ventilation is recommended; in event of skin contact, wash off promptly with soap and water.

TECHNICAL SERVICE

No one inhibitor or inhibitor-dispersant can fully and effectively protect every type of distillate fuel. Each needs its own proper inhibitor selection, which must be determined by a comprehensive analysis of the fuel to be treated. Universal therefore provides a series of four POLYFLO compounds, Nos. 100, 120, 121 and 130. The services of technically trained field men with years of experience in handling petroleum products are always available to users of POLYFLO 100 and other UOP products.

SHIPPING INFORMATION

Bill of Lading Description: "Fuel Oil Treating Compound for Preventing Precipitation of Sediment"

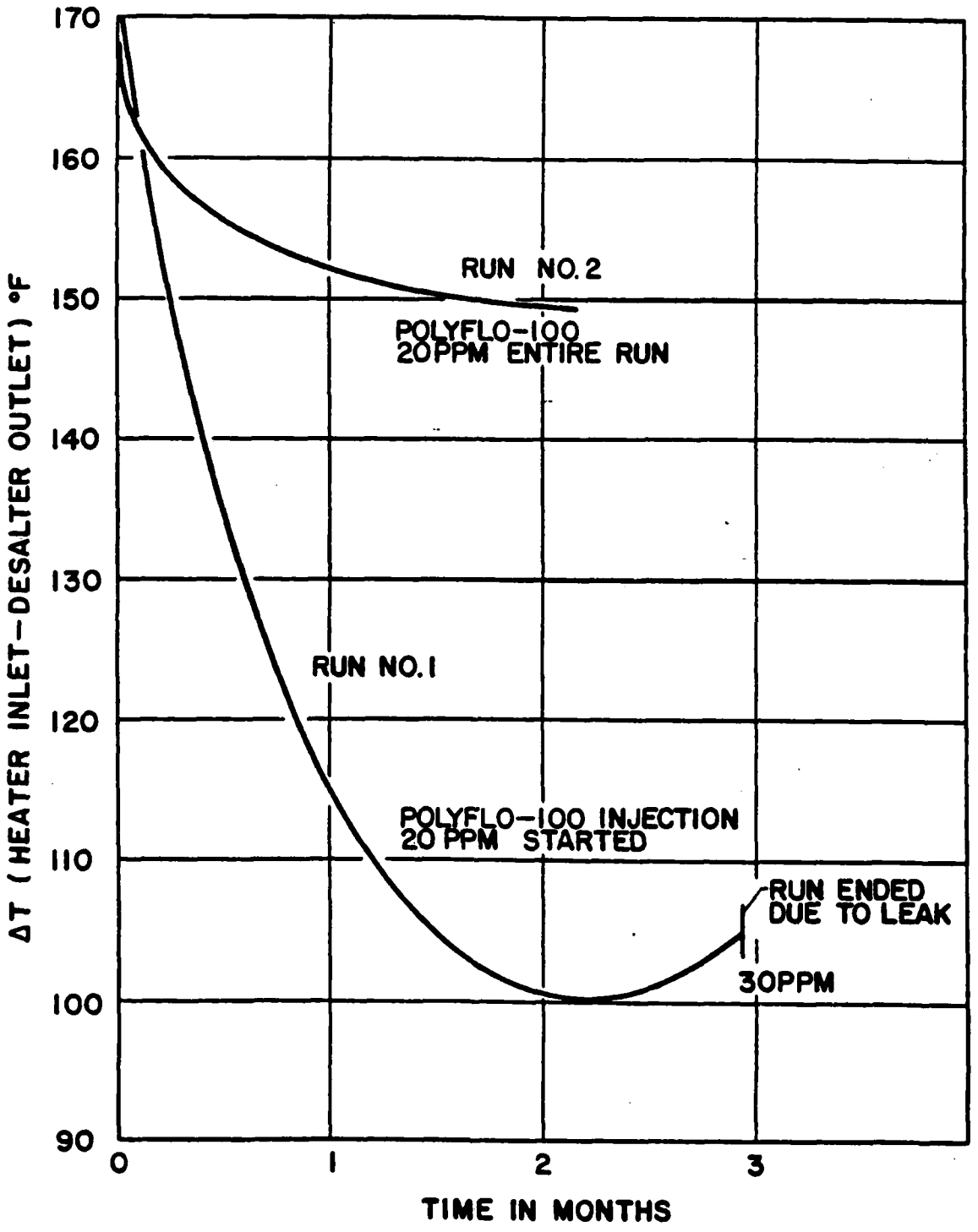
Containers: Non-returnable Steel Drums,
400 pounds net, 450 pounds gross weight

Warehouses:

Houston, Texas
Tulsa, Oklahoma
Long Beach, California
McCook, Illinois

March, 1967
T-367-B

EFFECT OF POLYFLOW IN PREVENTING FOULING IN A CRUDE OVERHEAD EXCHANGER



PROCESS DIVISION

technical bulletin

POLYFLO® 140

DISPERSANT-STABILIZER FOR DISTILLATE AND RESIDUAL FUELS

POLYFLO 140 is a new amine polymer having much improved physical properties when compared to certain other polymeric type dispersant-stabilizers. Its main functions are in the area of mitigating exchanger fouling and fuel oil stabilization with or without the auxiliary use of a Copper Deactiviator.

POLYFLO 140 in some cases functions as a pour point depressant in blends of No. 2 cycle oil and kerosine.

TYPICAL PHYSICAL PROPERTIES

Physical Form	Liquid
Gravity, °API at 60°F	24.0
Specific Gravity at 60°F	0.9100
Density at 15°C	0.9095
Weight at 60°F, lbs./gal	7.58
Pour Point, °F	below −85
Flash Point, T.O.C., °F	142
Flash Point, Pensky-Martens, °F	130
Viscosities:	
Kinematic at 60°F , cs	41.07
Kinematic at 100°F , cs	19.79
Universal at 60°F , secs	190.6
Universal at 100°F , secs	96.9
Universal at −33°F , secs	5000

DOSAGE

Antifoulant . . . . . 10-20 ppm
Fuel Oil Stabilizer . . . 15-40 ppm
Pour Point Improver. . . up to 1000 ppm

HANDLING

POLYFLO 140 is an organic base and should not be permitted to remain in contact with the skin but washed off immediately with soap and warm water. The eyes should be protected at all times.

CONTAINER

Non-returnable (55 gallon) steel drums, 400 pounds net weight.

WAREHOUSES

Houston, Texas
Tulsa, Oklahoma
Long Beach, California
McCook, Illinois

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Universal Oil Products Company
20 UOP Plaza—Algonquin & Mt. Prospect Roads
Des Plaines, Illinois 60016 312•391-2000

APPENDIX B

APPENDIX B: SOURCES OF INFORMATION

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369 Marshall Avenue
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Universal Oil Products, Inc.
Algonquin & Mt. Prospect Roads
20 UOP Plaza
Des Plaines, IL 60016

Mr. R. Rolland (312) 391-3407
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Mr. F. H. Franke (312) 391-2927
Monorex Instrumentation Division
Mr. R. Braun (312) 391-3341
Mr. C. A. Stansky (312) 391-2000

Government Laboratories and Divisions
U. S. Army Mobility Equipment Research & Development Command (MERADCOM)
Energy & Water Resources Laboratory
Fort Belvoir, VA 22060

Mr. Maurice E. LePera, Chief, Fuels * Lubricants Division, (703) 664-3576/4594
Mr. J. A. Christians, Chief, Energy & Water Research Laboratory, (703) 664-5696

APPENDIX C

APPENDIX C

SCOPE OF TASKS
TO
U. S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION (WES)[39]

1. PURPOSE:

The following tasks represent a preliminary of a long-range working relationship between the Huntsville Division (HND) and the U. S. Army Engineering Waterways Experiment Station (WES) for development of data and design criteria in support of the Regional Residual Storage Program (RPR) being developed under provisions of the Strategic Petroleum Reserve Program (SPR) for the Department of Energy (DOE).

2. TASK DESCRIPTIONS:

   a. Conduct search for data desired by DOE regarding additives used in various petroleum products, specifically residual fuel oils, jet fuels and naptha, and outlined in Attachment No. 1.

   b. Suggested sources of information are provided; however, research should not be limited to these sources.

3. SCHEDULE:

   a. The completion date for the completed Program Plan for the Department of Energy Regional and Noncontiguous Storage Plan is 31 May 1980.

   b. The referenced tasks are necessary to support the final preparation of the Program Plan.

   c. It is imperative that these tasks proceed immediately and with sufficient resourses to be completed 21 April 1980.

APPENDIX D

APPENDIX D

(Generalized

Use of Additives in Various Products

1. Residual Fuel Oils
   a. Pour Point Depressants
   b. Dispersants
   c. Corrosion Inhibitors
   d. Oxidation Inhibitors
   e. Metal Deactivators
   f. Others, if any

   Points of concern:

   Appropriate additives, long-term stability, effectiveness sensitivity to heating, undesirable effects and treatment costs and rates.

2. Jet Fuel
   a. Antioxidants
   b. Metal Deactivators
   c. Corrosion inhibitors
   d. Freeze inhibitors
   e. Other, if any

   Points of concern:

   Appropriate additives, storage stability, treatment rates and cost, and what additives currently used in Hawaii.

3. Naphthas

   Apparently little attention has even been given to the use of additives in naphthas. They are "unfinished oils" and are not stored for prolonged periods. Given the specifications for the two napthas to be stored, what additives would be appropriate; what is their long-term stability; and what is the dosage cost. There is an indication that naphthas are moderately corrosive, possibly necessitating the use of a corrosion inhibitor.


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